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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for U. S. ATOMIC ENERGY COMMISSION
by ARGONNE NATIONAL LABORATORY

● APRIL 1960

● VOLUME 3

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foreword

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the U. S. Atomic Energy Commission, Division of Information Services. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are L. Burris, Jr., A. A. Chilenskas, I. G. Dillon, A. A. Jonke, S. Lawroski, W. J. Mecham, W. A. Rodger, W. B. Seefeldt, and V. G. Trice. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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REACTOR FUEL PROCESSING

COMMERCIAL ASPECTS OF FUEL PROCESSING

Euratom Research and Development Authorization

The U. S.-Euratom Joint Research and Development Board announced that 23 contracts for research and development work totaling approximately $3.5 million have been authorized within the European Atomic Energy Community and the United States during the past six months.[1] During this initial period the Board concentrated its efforts chiefly on proposals related to the nuclear fuel cycle. Fourteen Community and eight U. S. organizations are represented by the work authorized, much of which involves close collaboration between Community and U. S. industrial groups. Approximately half of the funds have been awarded to Community and half to U. S. groups.

Only two of these awards were in the area of chemical processing:

1. Processing of irradiated uranium, submitted by Centre d'Étude de l'Énergie Nucléaire (CEN), Société Belge de l'Azote et des Produits Chimiques de Marly (SBAPCM), and Société d'Étude de Recherches et d'Applications pour l'Industrie (SERAI), Belgium.

2. Treatment of water and radioactive residues, submitted by Centre d'Étude de l'Energie Nucléaire and Evence Coppee, Belgium.

New Lease Agreement

The AEC published in the Federal Register[2] on Dec. 16, 1959, notice of intention to institute new lease agreements for all special nuclear material distributed by the Commission pursuant to Section 53 of the Atomic Energy Act of 1954. Copies of this new agreement may be obtained from Oak Ridge Operations Office, U. S. Atomic Energy Commission, Attn: AEC Materials Leasing Office, P. O. Box E, Oak Ridge, Tenn.

The system for distributing special nuclear material under the new lease agreement will differ from present Commission practice in that a single agreement, signed by the lessee and the Commission, will set forth the terms and conditions for all special nuclear material transactions for the account of the lessee. The terms and conditions for the majority of special nuclear material transfers are stated in the AEC Special Nuclear Material Order Forms and Transfer Forms covering such individual transfers. These forms will be discontinued when the new lease agreement becomes effective.

The new agreements were originally to go into effect on Feb. 1, 1960, but this date was subsequently changed to Mar. 1, 1960, by the AEC.[3]

Under the postponement, the new lease agreement must be executed by each licensee desiring to assume the lease responsibilities for special nuclear material to be received either directly from the Commission or from another licensee after Feb. 29, 1960. Previously, this date was Jan. 31, 1960.

Coincident with the use of the new lease agreement, the Commission is centralizing the administrative functions of leasing special nuclear material in the Oak Ridge Operations Office.

AEC Chemical Processing Services

The AEC has also announced some changes in the terms of arrangements for providing chemical-processing services for spent power-reactor fuels.[4] The more important changes reduce the minimum "turnaround" time from three

to two days and further permit the combining of batches to minimize further the turnaround charges.

The AEC, in its Annual Report to Congress[5] Jan. 30, 1960, announced changes in its schedule for the interim processing program. The announced schedule is as follows:

> The Commission, in a cooperative program with major reactor owners, expanded its studies on feasibility and design of relatively small chemical processing facilities which could be owned and operated privately. It postponed for a period of six months (to June 1960) modifications to Commission plants under the interim processing program to give further assurance to private processors that it will not compete in processing nonweapon fuels if industry does go forward with private plants.

Uranium Procurement and Production Statistics

The AEC has made public additional statistics on domestic uranium production and ore reserves spanning the fiscal years 1948 to 1959. The figures include uranium ore production, ore reserves, concentrate purchases, exploratory drilling, bonus payments, ore fed to process, and related subjects.[6]

Only 54,000 tons of uranium ore was produced in the western United States in the fiscal year 1948, as compared with more than 6 million tons in 1959. Domestic ore reserves in 1948 were estimated to be about 1 million tons, as against 86.1 million tons in 1959.

Ore reserve estimates, determined by the Commission, the U. S. Geological Survey, and the U. S. Bureau of Mines, are shown in Table I-1.

Increasing uranium ore production in the western states over the fiscal years 1948 to 1959 is shown in Table I-2.

In the 12 fiscal years from 1948 to 1959, the AEC incurred costs of $888 million in connection with the procurement of uranium concentrate (U_3O_8) from domestic sources. Table I-3 shows the total and average cost incurred by fiscal years. The costs shown include purchases from private producers, costs of operation of the AEC-owned mill at Monticello, Utah, and of weighing, sampling, and assaying, but exclude depreciation on AEC-owned facilities, bonus payments for initial ore production, and vanadium purchases.

Table I-1 U. S. URANIUM ORE RESERVE ESTIMATES[6]

Year*	Thousands of tons
1948 (January)	1,000
1949	1,000
1950 (July)	2,000
1951	2,000
1952	3,000
1953	5,000
1954	10,000
1955	27,000
1956	63,000
1957	78,000
1958	82,500
1959 (July)	88,900

*Year-end unless otherwise noted.

Table I-2 U. S. URANIUM ORE PRODUCTION,[6] 1948 TO 1959

Fiscal year	Dry tons	Per Cent U_3O_8
1948	54,000	0.31
1949	89,000	0.27
1950	230,000	0.31
1951	290,000	0.32
1952	390,000	0.32
1953	610,000	0.31
1954	914,000	0.32
1955	1,306,000	0.30
1956	2,185,000	0.28
1957	3,303,000	0.28
1958	4,416,000	0.27
1959	6,117,000	0.26

Table I-3 AEC PURCHASES OF DOMESTIC URANIUM CONCENTRATE[6]

Fiscal year	Total (millions)	Average cost per pound
1948	$ 1.7	$ 7.14
1949	2.0	8.53
1950	5.8	8.92
1951	12.8	10.01
1952	18.4	11.19
1953	24.2	12.30
1954	35.6	12.25
1955	53.6	12.51
1956	97.8	11.63
1957	159.6	10.53
1958	196.0	9.57
1959	280.5	9.25
Total	$888.0	$10.14

The AEC also announced[7] that it will not be in a position to exercise its options to purchase additional Canadian uranium concentrate in the post-1962 period but has agreed to a stretch-out

arrangement with Canada during the period Mar. 31, 1962, to Dec. 31, 1966.

Under the stretch-out agreement, the Commission's total Canadian uranium commitment remains unchanged with respect to the pounds to be delivered and the prices to be paid under existing contracts.

Under contracts with Canada, which expire Mar. 31, 1962, and Mar. 31, 1963, the Commission had the option until Mar. 31, 1961, of extending its purchases through Dec. 31, 1966, at $8 (U. S.) per pound of U_3O_8 in mill concentrate. The Commission has had a separate contract with Eldorado Mining and Refining Limited, a Canadian Government corporation, for each contract that Eldorado has with individual operators. The new plan provides for a single contract between the Commission and Eldorado covering the total commitment, instead of a number of contracts.

The Canadian Government will propose to the Canadian industry a plan which will permit the deferment of a portion of currently scheduled deliveries of uranium to the Commission until the 1962 to 1966 period. Because the deferred production had been counted upon by companies to provide amortization payments due in the pre-1962 period, an advance payment of $2.50 per pound of U_3O_8 will be made by the Commission to Eldorado, with respect to each pound deferred. These advance payments will be made at approximately the same time as the delivery of these pounds of U_3O_8 would have been made had there been no deferment.

New York State's Plans

On Dec. 3, 1959, New York State Governor Nelson Rockefeller sent to state legislative leaders proposed legislation which would direct the state's Office of Atomic Development to locate the following within the state, in the interest of attracting industrial nuclear installations:[8]

1. "Sites at which radioactive by-products could be concentrated and stored," such sites possibly to be acquired by the state or federal government.

2. "Sites at which an atomic test reactor could be constructed and operated," as a prerequisite to possible construction of a reactor by industry or the federal government.

3. "Port facilities capable of handling the fueling and servicing of atomic propelled vessels and the shipping of used uranium fuel."

Legislation was also recommended which would:

1. Direct the Office of Atomic Development to cooperate with appropriate federal, state, and local government agencies in establishing training programs for the handling of accidents, fires, or disasters believed to involve radioactive materials.

2. Direct the Office of Atomic Development to prepare, for state-wide distribution, a roster of persons within the state qualified in the detection and handling of radiation hazards, and a list of the type and location of technical equipment which could be useful in any radiation accident.

3. Authorize the Governor to enter agreements with the federal government to "assume regulatory authority over atomic by-product materials, source materials, and special nuclear materials in quantities not sufficient to form a critical mass."

4. Authorize the Office of Atomic Development to enter agreements with the federal government for performance on a cooperative basis of inspections or "other functions with respect to atomic energy activities within the state."

5. Authorize the state Department of Health to license the use of atomic energy materials.

An appropriation of $147,000 was proposed to carry out the recommended projects.

Reprocessing Study Group

The Davison Chemical Division of W. R. Grace and Co. recently joined five utilities to form a new organization known as the Industrial Reprocessing Group, to undertake a privately financed $250,000 study of the technical and economic feasibility of designing, building, and operating a privately owned facility for the processing of spent nuclear fuels.[9] The utilities are: Commonwealth Edison Co., Consolidated Edison Co., Detroit Edison Co., Northern States Power Co., and Yankee Atomic Electric Co. Davison will direct the six-month study of all cost factors connected with the differing types of fuel used in the five reactors. The AEC, which now performs all nuclear fuel processing, has agreed to provide the group with relevant information.

Waste-disposal Licensing

Hearing on the application of Walker Trucking Company of New Britain, Conn., for a license amendment authorizing use of a site in New Britain in connection with sea disposal of low-level atomic wastes[10,11] was to be resumed on Feb. 9, 1960. Walker Trucking Company has applied for a license amendment which would allow use of a site in New Britain, owned by the company, for encasing the packages in concrete preliminary to their disposal at sea. At a public hearing on this application held June 3, 1959, in New Britain, a group of citizens, represented by counsel, and the mayor of New Britain appeared as intervenors. After the taking of direct testimony on behalf of the applicant and the AEC staff, the hearing was recessed.

Oral argument before the Commissioners in the Industrial Waste Disposal Case, to which objection has been raised by Harris County (Houston, Texas), the Government of Mexico, and several others was postponed[12,13] from Dec. 17, 1959, to Jan. 20, 1960.

The AEC has also issued letter orders to five additional uranium processing mills directing them to take prompt steps to correct apparent violations of the Commission's radiation-safety regulations.[14] All five companies were directed to submit, by Nov. 30, 1959, a full statement of the corrective steps taken and to be taken to bring their operations into such compliance. In addition, each company was directed to submit at the end of December 1959, and monthly thereafter, a report on its radiation program which is to include a listing of deficiencies remaining to be corrected and steps taken to correct deficiencies, including installation of equipment as required.

The companies to which the letter orders were directed are: Union Carbide Nuclear Co., New York, operating a mill at Rifle, Colo.; Rare Metals Corporation of America, Salt Lake City, Utah, operating a mill at Yuba City, Ariz.; Dawn Mining Co., New York, operating a mill at Ford, Wash.; Gunnison Mining Co., Gunnison, Colo., operating a mill at Gunnison, Colo.; Mines Development, Inc., Denver, Colo., operating a mill at Edgemont, S. D.

Apparent violations cited in the letter orders follow:

Union Carbide Nuclear Co.: Exposed employees to dust containing concentrations of air-borne radioactive material in excess of limits; failed to conduct adequate surveys in all mill areas occupied by employees to determine concentrations of air-borne radioactivity; failed to determine concentrations of radioactive material, including radium, entering the Colorado River from the tailings pond; failed to post air-borne radioactivity areas; failed to post entrances to the mill conspicuously as required by license.

Rare Metals Corporation of America: Exposed employees to dust containing concentrations of air-borne radioactive material in excess of limits; failed to conduct adequate surveys in all mill areas occupied by employees to determine concentrations of air-borne radioactivity; records of surveys that were taken were not maintained in the same units as required by regulations.

Dawn Mining Co.: Failed to conduct surveys in mill areas occupied by employees to determine concentrations of air-borne radioactivity; failed to post radiation areas; failed to maintain complete records of external radiation surveys.

Gunnison Mining Co.: Failed to conduct adequate surveys in mill areas occupied by employees to determine concentrations of air-borne radioactivity; failed to post entrances to mill conspicuously as required by license; failed to maintain records of radiation surveys.

Mines Development, Inc.: Failed to conduct surveys in mill areas occupied by employees to determine concentrations of air-borne radioactivity; failed to conduct adequate surveys in mill areas occupied by employees to determine external radiation levels.

Issuance of the orders brings to 11 the number of mills which have received letter orders as a result of a program of inspections being carried out by the Commission.

References

1. Euratom Joint Research and Development Board Announces Authorizations Made During Past Six Months, AEC Press Release B-235, Dec. 22, 1959.
2. *Federal Register* Doc. 10638, Dec. 16, 1959.
3. AEC Press Release IN-46, Jan. 12, 1960.
4. *Federal Register* Doc. 10639, Dec. 16, 1959.
5. AEC Annual Report to Congress, Jan. 30, 1960.
6. Additional Uranium Statistics for Fiscal 1948–1959 Announced by Atomic Energy Commission, AEC Press Release B-223, Dec. 1, 1959.

7. U. S. Will Not Exercise Uranium Options with Canada, Plans Stretch-Out Through 1962–1966 Period, AEC Press Release B-204, Nov. 6, 1959.
8. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 6(12): (December 1959).
9. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., 7(1): (January 1960).
10. *Reactor Fuel Processing*, 2(1): (January 1959).
11. License Hearing to Resume in New Britain, Conn., AEC Press Release B-238, Dec. 22, 1959.
12. *Reactor Fuel Processing*, 3(1): (January 1960).
13. AEC Postpones Oral Argument in Waste Disposal Case, AEC Press Release B-221, Nov. 23, 1959.
14. AEC Issues Letter Orders to Five Additional Uranium Mills, AEC Press Release B-206, Nov. 10, 1959.

Two incidents affecting safety in chemical-processing plants have occurred recently, one at Oak Ridge and one at Idaho.

The Oak Ridge accident[1] occurred on November 20 in the Thorex Pilot Plant in a cell which had been used for processing highly radioactive waste products to recover plutonium and other transuranium elements contained in the waste. A recent report (as yet unpublished) by the ORNL investigating committee (C. E. Winters, Chairman; K. A. Kraus; and A. C. Upton) describes the events leading up to the accident and makes several recommendations to prevent the recurrence of such an accident. A more detailed discussion of this incident has been presented[2] in *Nuclear Safety*, Vol. 1, No. 3.

The processing run had been completed, and the cell was undergoing cleanup when the accident occurred. No detailed examination of the cell and the equipment has been made to date, but strong circumstantial evidence points to an evaporator which at the time of the accident was being decontaminated with a solvent containing organic additive. The decontamination procedure included a step involving addition of dilute nitric acid (20 per cent) and boiling off the nitric acid (a concentrating step). Other organics may have also been present and entered into the explosion which occurred after conclusion of the distillation (~70 vol.% of nitric acid distilled off) when the operator had started to drain the evaporator. The explosion blew open the cell door and scattered approximately 600 mg of plutonium over some of the nearby areas. Roughly four acres, including roof areas, were affected. No one was injured in the explosion, and no overexposures to radiation resulted.

The explosion resulted in loss of equipment in the cell valued at $10,000. The cell remains inaccessible to cleanup crews because of the high levels of gamma radiation resulting from the waste material which had been processed.

Decontamination of the area has involved painting and cleaning buildings; replacement of about 100 yards of asphalt roadway; spraying the roof of one building with asphalt and tar; painting roofs of two other buildings with enamel paint; and removal of grass and resodding of one-eighth acre of ground. Three trucks were parked nearby when the accident occurred. Two of these, both 1952 models, have been discarded; the third, a 1956 model, has been cleaned and is back in service. The cost of decontamination when completed is expected to range from $250,000 to $350,000.

Although some areas in the Laboratory are still on a limited-access basis because of contamination, all of the affected area except the cell in the Thorex Pilot Plant was to have been cleared by February 15.

The incident at Idaho occurred on Oct. 16, 1959, and involved an accidental criticality. The summary of the preliminary report of the investigating committee follows:[3]

> At approximately 0250 Friday, Oct. 16, 1959, a nuclear incident occurred in a process-equipment waste-collection tank at the Idaho Chemical Processing Plant, National Reactor Testing Station. Radiation alarms in the plant were set off by the resulting release of air-borne radioactivity, and 21 shift workers and security personnel on duty evacuated the process building and the surrounding area of high radioactivity.
>
> Available evidence indicates the critical condition resulted from the accidental transfer of a concentrated uranyl nitrate solution from geometrically safe storage tanks into a waste-collection tank through a line normally used to transfer decontaminating solutions to waste. Siphon action initiated by air sparging appears to be the most likely mechanism by which the transfer took place.
>
> Of the 21 personnel directly involved in this incident, only seven received significant external exposure to radiation. Of the seven only two exceeded the year's maximum permissible exposure of 30 rem to the skin (individual exposures of 50 and 32 rem), and none received a year's maximum permissible exposure of 15 rem penetrating radiation (highest received was 8 rem). No medical treatment was required. The waste-collection tanks are approximately 50 ft below grade with a 4-ft-thick concrete deck over the vessels. This effectively prevented the escape of fission neutrons or gamma radiation from the reaction into operating areas.

Limited visual inspection and tests indicate that no significant property damage resulted from this occurrence, and the losses will be restricted to the cost of recovering contaminated uranium solutions resulting from the incident. It is estimated that total costs directly resulting from the incident will not exceed $100,000. Reliable uranium material balance data must await completion of recovery processing of the solutions involved.

The magnitude of the excursion has been set at 4×10^{19} fissions, based primarily upon radiochemical analysis for Mo^{99} in the resulting solution. A neutron-flux density of approximately 1.5×10^{13} neutrons/cm^2 was estimated by Fe^{59} and Co^{58} activity in a stainless-steel nut and bolt obtained from the vicinity of the reaction. The reaction is thought to have occurred in a system containing approximately 34 kg of highly enriched uranium in about 800 liters of total solution. There were no radiation detectors located in the tank cell because of the normally high background radiation present. It is likely that gaseous and air-borne contamination moved out via vent lines and drain connections into operating areas where continuous air monitors and radiation-level monitors were located. The nuclear burst and pressure wave back through the waste system, and possibly through the vessel off-gas system, spread activity through the building in a path from bottom to top and generally from south to north, triggering radiation alarms and prompting evacuation of the building.

The process building was evacuated within about 2 min after establishment of an emergency condition. Outside the building and for 130 yards west to the area entrance, the radiation field was 5 r/hr or greater. Personnel were evacuated to the MTR/ETR area (2 miles west).

Following the evacuation and the dissipation of the high levels of air-borne activity, personnel reentered the building approximately 45 min after the incident and accomplished an orderly shutdown of equipment.

References

1. ORNL Decontamination To Be Completed by February 15, AEC Press Release C-14, Jan. 30, 1960.
2. *Nuclear Safety*, 1(3): 78 (March 1960).
3. W. L. Ginkel et al., Report of Investigating Committee, Idaho Operations Office, Nov. 16, 1959.

Mechanical Processing

Many of the newer fuels are clad with materials that may be dissolved only with difficulty. However, the removal or destruction of the cladding by mechanical means will sometimes permit conventional nitric acid dissolution of the fuel material. Studies of shearing and sawing methods are continuing at Hanford.[1-3] Sawing methods include cold sawing and hack sawing. Figures 1 and 2 show the cold saw and coldsaw blade used in hardware cutoff studies. Comparison of coldsawing and hacksawing techniques applied to simulated hardware has shown that:[1]

1. The cold saw, being a simpler mechanism, is more adaptable mechanically for remote cell service.

2. The hack saw, using a "two-piece" blade,* is a serious competitor of the cold saw.

3. Both saws require special clamping fixtures (i.e., "combs" for rod bundles), but hacksaw clamping requirements are less rigorous than those for the cold saw.

4. Coldsaw chips are larger than hacksaw chips, but chips from either may be collected by simple screens. Pyrophoric hazards will be negligible for underwater storage.

5. Water-lubricated cutting (minus conventional lubrication cutting oils which might adversely affect subsequent solvent extraction) will not affect blade life significantly for either saw.

A power hack saw employing a two-piece blade has been selected for inclusion in the mechanical cell of the nonproduction fuels processing program.[2] The selection was based upon the following major factors: (1) adequate performance demonstrated in cutting "hardware" typical of that encountered in the fuels to be processed at Hanford; (2) low equipment and blade replacement costs; and (3) production of easily handled fines with a relatively low pyrophoric hazard.

Difficulties have been encountered when sawing unsupported rod sections (away from tube sheets) of multirod bundles. Blade breakage has resulted when the cut tubes are free to vibrate and bind the saw blade. A "potting" technique has been investigated as a method of firming up an unclampable bundle. The section to be cut is cast in plaster-of-Paris, after which it can be easily cut by the hack saw without noticeable blade damage. Figure 3 shows a cross-section cut made of a potted Dresden prototype fuel.

Two additional types of hack saws, a "dual-feed" Marvel* (Fig. 4 shows the Marvel saw, which is similar to the hack saws found in many metal shops) and a simpler, less expensive Peerless† have been used to saw thin-walled tubes and rod bundles with springs,[2] simulating Piqua and Dresden fuels, respectively. The following observations were made:

1. With either saw, one rugged "weld-edge" (two-piece) blade may be expected to remove the end hardware from fuel elements containing at least a ton of uranium. This estimate assumes that rod bundles will be sawed through at massive end-plate sections rather than through unsupported rod sections. The resultant blade cost is approximately $3.

2. Blade life is equal for either saw, and imperfections in "as-received" blades (indicated by porosity, cracks, and poor weld bonds revealed in radiographic and dye penetrant tests) have negligible effect on blade life.

Knife and sabersaw cutting of thin stainless-steel bands, such as those used to hold the subassemblies of the Yankee fuel together, was attempted.[3] Some knife jamming occurred because of band movement during the cutting operation. A weld-edge saber saw was successful in band cutting, but excessive blade vibration occurred with cuts made deep within a bundle, i.e., 6 to 7 in.

*The two-piece blade shown in Fig. 3 consists of a row of hardened steel teeth backed up by an integral tough steel backup plate.[4] When the blades are used, blade breakage is very low compared to "one-piece" conventional blades.

*Armstrong-Blum Mfg. Co., Chicago, Ill.

†Peerless Machine Co., Racine, Wis.

Figure 1 — Cold saw used in hardware cutoff studies.[4]

Figure 2 — Coldsaw blade used in hardware cutoff studies.[4]

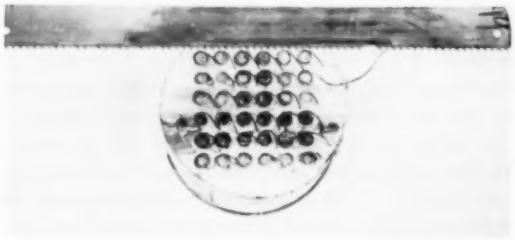

Figure 3 — Two-piece hacksaw blade used in hardware cutoff studies, showing a cut cross section of potted Dresden prototype fuel.[4]

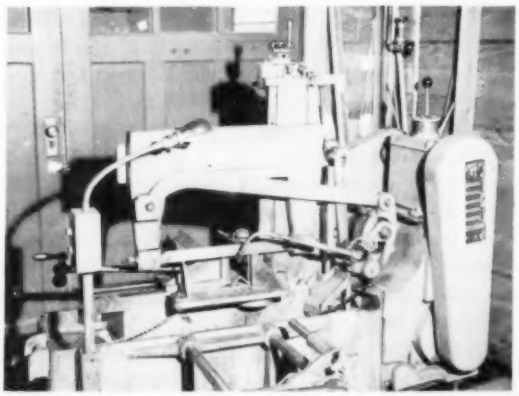

Figure 4 — Marvel hack saw used in hardware cutting studies.[4]

Underwater shearing of swaged uranium dioxide fuel elements is being investigated[2] to determine the nature and extent of contamination of the basin water with uranium dioxide particulates. About 2 per cent of the uranium dioxide is less than 200 mesh and is readily dispersed and suspended in the basin water. Approximately 0.04 per cent of the uranium dioxide is finer than 3 μ and has a very low settling rate. Unclad sintered uranium dioxide pellets were also sheared under water.[3] Slurried fines (<200 mesh) amounted to less than 1 per cent of the material processed.

The basin water was cleaned with a filter and with a commercial 3-in.-diameter hydroclone. The filter (1 sq ft in area, 45-μ pore size) removed essentially all the uranium dioxide but plugged quickly (approximately 4 lb of uranium collected). The hydroclone was effective in re-

moving only the larger solids (greater than 5 μ) in the feed, and a cloudy overflow discharge resulted. A $1\frac{1}{2}$-in.-diameter hydroclone has given removal efficiencies as high as 50 per cent using a fine lead oxide powder slurry as a stand-in for uranium dioxide slurries. A concentration factor (underflow concentration/overflow concentration) of 25 and a 25 per cent removal efficiency have been achieved at an overflow-to-underflow volume ratio of 80.

At Oak Ridge National Laboratory (ORNL) the mechanical processing of Sodium Reactor Experiment (SRE) fuel (uranium rods in stainless-steel tubes) is being studied.[5] A rotary slug washer to move NaK was tested with nonradioactive material. The slug basket rotated at 1000 to 1650 rpm and consumed ~3 lb of steam per minute (30 to 40 psig). About 10 min was required to ensure removal of NaK and oil.

In the shearing tests on stainless-steel-clad porcelain-filled prototype fuel at ORNL and under two subcontracts, a stepped punch working against a circular anvil or a V-shaped anvil appeared superior to the other combinations tested[5] because it produced maximum breakage of core material, required lower tonnage, and gave the best separation at ferrule locations. For the three test programs, approximately 85 per cent of the porcelain dislodged was 1700 μ or less in size, and 12 to 27 per cent was 100 μ or less. It is estimated that a stepped blade shearing uranium dioxide into 1-in. lengths under conditions similar to those used for shearing porcelain would dislodge approximately 50 per cent of the uranium dioxide present. Dislodgement of the ceramic was minimum with a blade clearance of 5 mils and a bundle orientation that gave maximum support to the individual tubes of a bundle. Increasing the blade velocity probably increased the amount of fines dislodged from that normally obtained with a sharp-edged blade.

Chemical Dejacketing

Selective chemical dissolution of fuel jackets and structural components is an alternate to mechanical dejacketing or complete dissolution. The exposed fuel cores can then be dissolved by another reagent in a second step. The principal jacket materials are aluminum, zirconium or Zircaloy, and stainless steel. Nickel coatings for aluminum jackets have also been proposed.

Removal of Zirconium and Zircaloy Jackets

The Zirflex process (ammonium fluoride–ammonium nitrate) may be used to remove zirconium or Zircaloy cladding from fuel elements having either oxide or uranium-niobium-zirconium alloy cores. Studies at HAPO[1–3] on the stability (toward solids formation) of solvent-extraction feeds that were prepared following a Zirflex decladding show the desirability of minimizing the amount of decladding solution carried forward into the core dissolver solution.

Trace concentrations of sodium ion do not affect the dissolution rate of Zircaloy-2 in 4*M* ammonium fluoride–0.5*M* ammonium nitrate, but concentrations in excess of 0.1*M* reduce the dissolution rate markedly. Up to 0.1*M* sodium, dissolution rates were in excess of 25 mils/hr; from 0.15*M* to 0.50*M* sodium, dissolution rates decreased from 2.9 mils/hr to 0.25 mil/hr.

Two batch Zirflex dissolutions were made at HAPO in the blanked-off reservoir of the recirculating tube dissolver.[3] In the first run, 1.75-in.-ID by 8-ft-long 55-mil Zircaloy tubing was dissolved in 6*M* ammonium fluoride–0.55*M* ammonium nitrate using a fluoride-to-zirconium mole charge ratio of 7. A maximum dissolution rate of 60 mils/hr and an integrated dissolution rate of 15 mils/hr was obtained. In a second similar run, 3-ft-long elements consisting of 1.1-in.-OD Zircaloy-2-clad uranium rods encircled by 1.62-in.-ID Zircaloy-2 tubes coated on the outside with plastic were dissolved at a maximum rate of 63 mils/hr and an integrated rate of >15 mils/hr.

Some modified-Zirflex-process flow sheets are being developed at ORNL for processing power-reactor fuel alloys.[6] An alloy of 1 per cent uranium–97 per cent zirconium–2 per cent tin and Experimental Boiling Water Reactor (EBWR) Core 1 (93.5 per cent uranium–5 per cent zirconium–1.5 per cent niobium clad in Zircaloy-2) fuels are used as examples of low- and high-uranium fuels, respectively. A dissolvent of 6*M* ammonium fluoride yields a solution of zirconium and a precipitate of ammonium uranous fluoride. In one process (part *a* of Fig. 5), ammonium hydroxide is added to produce insoluble hydrous oxides of uranium, zirconium, and niobium. The ammonium fluoride–ammonium hydroxide supernatant is removed by filtration, partially evaporated, and recycled as dissolvent. The uranium and zirconium oxides are dissolved in nitric acid to yield a solvent-

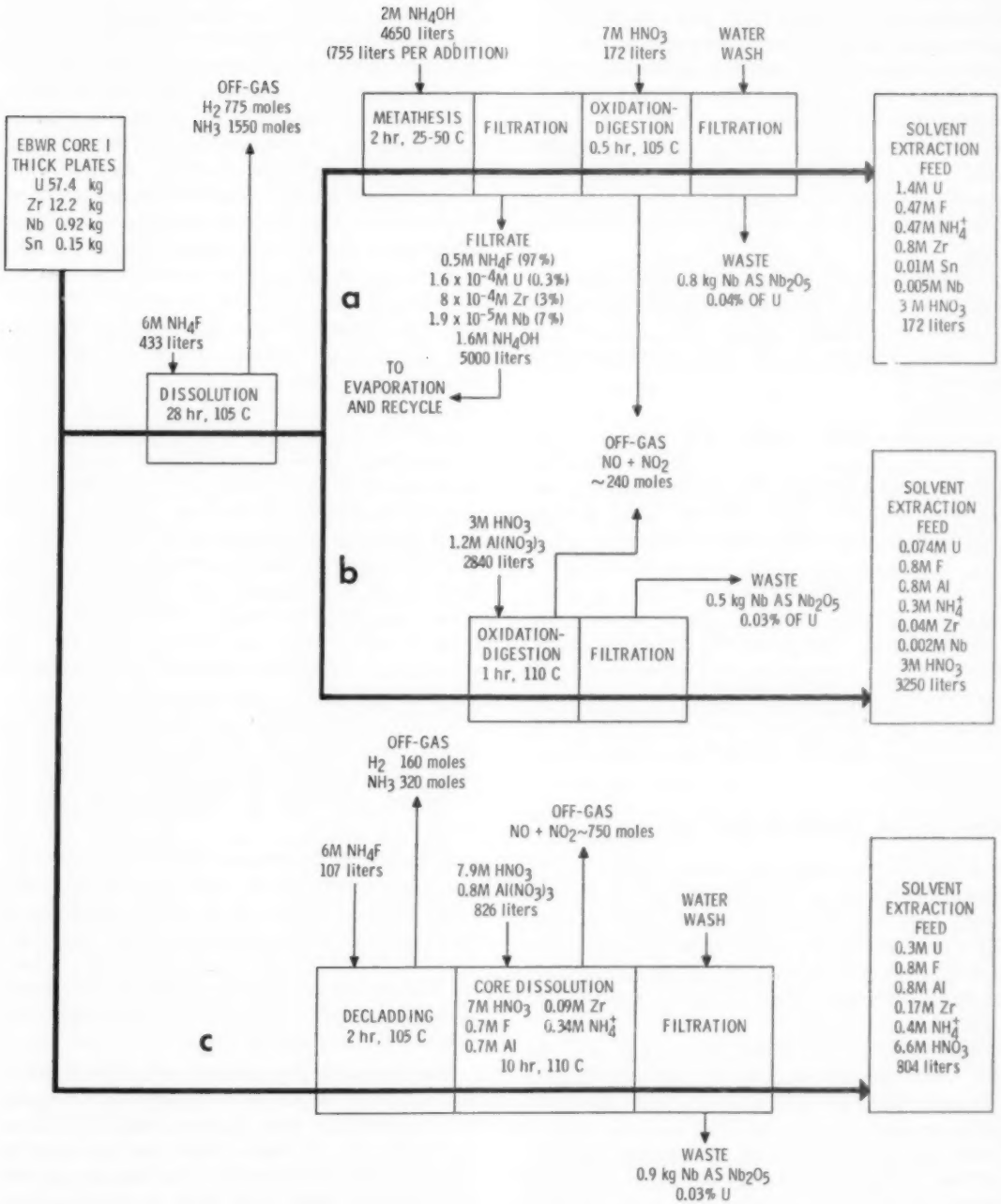

Figure 5—Modified Zirflex process for dissolution of high-uranium (EBWR Core 1) fuel in aqueous ammonium fluoride.[6] Solvent-extraction feed preparation was by (*a*) metathesis and nitric acid oxidation, (*b*) nitric acid oxidation, and (*c*) two-step dissolution of high uranium in aqueous fluoride. A similar flow sheet for low-uranium fuel was given in *Reactor Fuel Processing*, 2(3): 6 (July 1959).

extraction feed solution of low fluoride content. In an alternate process (part *b* of Fig. 5), nitric acid and aluminum nitrate are added to the ammonium fluoride fuel solution to oxidize U(IV) to soluble U(VI) and prepare a stable solution suitable for solvent extraction. In a variation of this flow sheet (part *c* of Fig. 5) for the EBWR fuel, only enough 6*M* ammonium fluoride is added to dissolve the cladding. Nitric acid and aluminum nitrate are then added to dissolve the core.

Zirconium alloys may also be dissolved electrolytically. Zirconium can be converted to ZrO_2 by anodic treatment in nitric acid.[7] The principal anode reaction at 60°C can be represented by

$$Zr + 2H_2O \rightarrow ZrO_2 + 4H^+ + 4e^-$$

The measured current efficiency of the reaction is usually greater than 100 per cent. This is thought to be due to the anode reaction

$$Zr + 2H_2O \xrightarrow{H^+} ZrO_2 + 2H_2$$

Preliminary work at the Savannah River Plant (SRP)[8] shows that zirconium metal and zirconium–10 per cent uranium alloy are electrolytically disintegrated in 8*M* to 13*M* nitric acid with a current utilization of 0.7 to 1.2 g/(amp)(hr).

Removal of Stainless-steel Jackets

A Sulfex flow sheet has been presented in an earlier Review[9] for Yankee Atomic Power Reactor fuel. Similar flow sheets have been developed at ORNL[10] for Consolidated Edison power-reactor fuel by removal of the stainless-steel cladding with 200 per cent excess of boiling 4*M* or 6*M* sulfuric acid.

Simulated Consolidated Edison fuel pins, 95 per cent thorium dioxide–5 per cent natural uranium (83 per cent of theoretical density), were irradiated to ~200 Mwd per ton of thorium, and the stainless-steel cladding was dissolved in boiling 6*M* sulfuric acid.[11] Loss of uranium, thorium, and plutonium to the decladding solution varied randomly from 0.07 to 1.5, 0.04 to 3.2, and 0.2 to 8.9 per cent, respectively, in decladding times of 0.5 to 3 hr. Most of the loss occurred in the first 30 min.

Additional Sulfex pilot runs were completed at HAPO.[2] There was no evidence of the reaction between 304-L stainless steel and about 2*M* sulfuric acid. In about 2.5*M* sulfuric acid the reaction started readily and proceeded uniformly at a rate of 6 to 8 mils/hr, slightly less than the rates attained in previously reported runs at acid concentrations of about 3.5*M* to 4.0*M* sulfuric acid. A bench-scale Sulfex run was made using a charge of 304-L stainless steel. The reaction was started in 4.0*M* sulfuric acid with the stainless steel in contact with carbon steel, after which the solution was diluted to 2*M* sulfuric acid. The dissolution proceeded uniformly at a rate of 4 to 6 mils/hr.

In work at ORNL[12] the time required to break the passivation of films on 304 stainless steel produced by a 1-hr treatment in refluxing 15.8*M* nitric acid–0.025*M* Cr(III) was shown to decrease as the sulfuric acid concentration increased and to increase greatly when nitric acid was added to the sulfuric acid. The films resisted refluxing 6*M* sulfuric acid for 7 min, 6*M* sulfuric acid–0.001*M* nitric acid for 2 hr, and 6*M* sulfuric acid–0.01*M* nitric acid for several days. In refluxing 12*M* sulfuric acid the films dissolved in about 10 sec with up to 0.001*M* nitric acid in the solution, but 0.5 hr was required with 0.01*M* nitric acid. The addition of 0.1*M* formic acid to refluxing sulfuric acid solution effectively destroyed as much as 0.01*M* nitric acid. Films on bundles of 304 stainless-steel tubes brazed together with Nicrobraze-50 dissolved instantly in refluxing 6*M* sulfuric acid.

Stainless steel was electrolytically dissolved at SRP[13] in nitric acid, with a tantalum basket serving as an inert electrical connector to the anode. An average of 0.7 g of stainless steel was anodically dissolved for each ampere-hour of charge through the cell. Arcing was minimized by use of an aluminum liner above the solution level in the basket.

The behavior of niobium as an inert metal connector to the anode for electrolytic dissolution of stainless steel is very similar to that of tantalum, but it costs about half as much as tantalum per unit volume. The dissolution rate of stainless steel was about 0.7 g/(amp)(hr) in laboratory tests at SRP[8] with the stainless steel in contact with an anode basket made of niobium and in a semiworks test using a consumable anode of stainless steel.

Electrolytic dissolution of stainless steel is also being studied at Idaho. Eleven steady-state

(constant solution composition) dissolution runs have been completed at the Idaho Chemical Processing Plant (ICPP)[14] in a 20-amp electrolytic dissolver with a variety of stainless-steel anodes as well as with Army Package Power Reactor (APPR) fuel strips. In four APPR runs, the uranium loss to the anode sludge ranged from 0.02 to 0.001 per cent. The anode sludge was appreciable, typically 2 per cent of the stainless steel dissolved. Particle size of the sludge was about 10 μ. About 1.3 moles of nitric acid was consumed per equivalent of metal dissolved. The corrosion of the Carpenter-20 cathode was 0.1 and 3 mg/(amp)(hr) at 0.5 and 1.5 amp/cm^2 current density, respectively.

Austenitic stainless steel was dissolved in 4*M* nitric acid at 20°C under an impressed anodic current to simulate raffinate from the electrolytic dissolution process. Type 304-L stainless-steel coupons were immersed in the raffinate for five 48-hr periods at 57 and 104°C. The rate of attack on the alloy was about 6.0 mils/month, with severe grain-boundary attack at 104°C. At 57°C the alloy completely resisted the effects of the corrodent raffinate.

Removal of Aluminum Jackets

The "as-deposited" nickel coating proposed at Hanford for aluminum-clad production fuels is a metastable phase.[1] At temperatures at or above 300°C, it transforms rapidly to a mixture of crystalline nickel and Ni_3P (phosphorus is deposited with the nickel from the plating bath). The equilibrium phase mixture dissolves much more rapidly than the as-deposited coating in dilute (1*M*) nitric acid. Observed dissolution rates for the equilibrated coating in boiling 1*M* nitric acid were about 0.15 g/(cm^2)(hr); rates for the as-deposited coating were about 0.006 g/(cm^2)(hr). Attempts to strip the as-deposited coating with sodium cyanide were not successful.

As noted previously, nickel coatings deposited on aluminum by the Kanigen process convert rapidly (5 min or less) to an equilibrium form when heated to 300°C or above.[2] Dissolution of coating in the equilibrated form occurs much more rapidly in dilute nitric acid than does the as-deposited form. A survey of equilibrated coating dissolution rate versus nitric acid concentration in the range 0*M* to 1*M* was made. Calculations based on these rate data, on similar rate data for the dissolution of ingot uranium, and on the surface area of uranium normally present in a dissolver heel indicate that a 0.5-mil coating could be removed in 1 hr in boiling dilute (<0.2*M*) nitric acid with a loss of uranium to the solution of less than 0.1 per cent of the heel.

Dissolution

Simultaneous Dissolution of Jacket and Core

1. *Zirconium Fuel Elements.* Further studies[2] on total dissolution of Zircaloy-2-clad fuels have sought to define solvent-extraction feed compositions stable toward solids formation. The procedure involves Zirflex dissolution of Zircaloy-2 cladding followed by uranium dioxide core dissolution through addition of nitric acid and aluminum nitrate. Stable feed solutions can be prepared from a Dresden fuel (or any other having a comparable mole ratio of Zircaloy-2 to uranium) with a uranium concentration of about 0.5*M*, a free-acid concentration of about 1*M*, and an aluminum-to-fluoride mole ratio of about 1. Higher aluminum-to-fluoride mole ratios or lower nitric acid concentrations result in precipitate formation.

A study of total dissolution of zirconium-clad uranium dioxide fuels and subsequent preparation of feed solutions suitable for Redox processing was initiated.[1] The scheme explored involved dissolution of the zirconium cladding by the Zirflex process and subsequent core dissolution without removing the decladding solution. Preliminary results indicate that stable (toward solids formation) solutions containing about 0.4*M* zirconium and less than 1*M* free nitric acid can be prepared by this scheme. Stability appeared to depend primarily on zirconium and free-acid concentration as expected. Rate of oxidation of Pu(IV) in the feed solutions was dependent on the aluminum-to-fluoride (free fluoride) mole ratio; a ratio of 2 or more was required for adequate oxidation of plutonium in 2 hr.

A tentative ORNL flow sheet is presented in Fig. 6 for the dissolution of 7 per cent uranium-zirconium-tin alloy in hydrogen fluoride–hydrogen peroxide[15] (Perflex process). A mixture of 34.4*M* hydrogen fluoride–0.6*M* hydrogen peroxide is fed to the dissolver at a controlled rate. All of the uranium and tin dissolves with the zirconium. Aluminum nitrate and nitric acid are added after dissolution to yield a stable

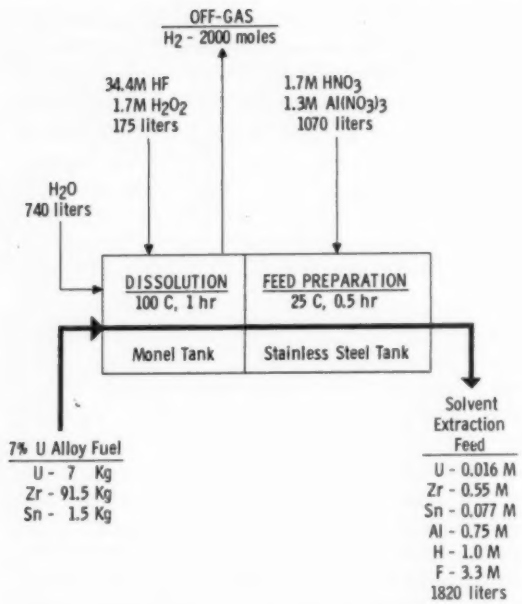

Figure 6 — Perflex process for dissolution of uranium-zirconium alloys in hydrofluoric acid–hydrogen peroxide.[15]

solvent-extraction feed solution which has a higher uranium concentration and the same zirconium, aluminum, and fluoride concentration as that presently used at the ICPP. Hastelloy-C appears to be the best construction material, with corrosion rates of approximately 0.08 mil/cycle for the unwelded metal. Niobium dissolves readily in hydrogen fluoride–hydrogen peroxide.

A flow sheet for dissolution of 7 per cent uranium-zirconium alloy in ammonium fluoride–hydrogen peroxide, in which uranium is not precipitated, was demonstrated on a laboratory scale[6] at ORNL. The dissolution time was 2 hr, and the uranium concentration in the dissolver solution was 0.0075*M*. Titanium is protected by the presence of uranyl ion in this solution to a greater extent than is Zircaloy-2, but this protection is not sufficient to permit use of titanium equipment for the process.

A modified Zirflex process has been proposed at ICPP.[16] It is a combination of a Zirflex dissolution (NH_4F) of the zirconium fuel, in which only a few per cent of the uranium dissolves, followed by precipitation of the zirconium and fluoride from the dissolver solution as barium fluozirconate.

Studies of the rate of dissolution of zirconium alloy (Zircaloy-2) in hydrofluoric acid–nitric acid are also being made at ICPP.[16] The initial rate of dissolution is directly proportional to the initial hydrofluoric acid concentration as previously reported, and the rate constant for the expression $d(\mathrm{Zr})/dt = k(\mathrm{HF})$ is 88 mg/(cm^2 Zr)(min)(mole HF)/liter for 8*M* nitric acid at reflux (108°C) and in the range of 0.1*M* to 1.5*M* hydrofluoric acid.

Dissolution of zirconium-base fuel elements by a salt-phase chlorination process is proposed.[17] Lead chloride rapidly dissolves zirconium, Zircaloy-2, and uranium-zirconium alloys; zirconium tetrachloride readily volatilizes from the melt; and uranium loss by volatility can be reduced to a negligible amount. Salient advantages offered by this process, called the Alloy Reguline Chloride Oxidation (ARCO) process, include early separation of matrix material simultaneously with dissolution, reduction in size of final uranium decontamination equipment, and compact waste storage.

The salt matrix produced in the ARCO process can be readily dissolved by refluxing in concentrated nitric acid and subsequent dilution of the slurry to 2*M* nitric acid.[14,16] Uranium losses for the entire dissolution are less than 0.5 per cent. Dissolutions of irradiated coupons were completed[18] on a 100-g scale at a temperature of 520°C. No nitric acid insoluble residues were found in the salt product. Most of the cesium, strontium, and cerium remained in the salt phase as expected; ruthenium favored the lead phase in two of three experiments. Although other molten chlorides were investigated, none proved better than lead chloride. Corrosion studies indicated two alloys (Incoloy-804 and Carpenter-20) with encouragingly low corrosion rates (3 to 6 mils/month) for this type of process.

An investigation of the lead-rich portion of the UCl_4-$PbCl_2$ system is near completion.[14] The thermal-arrest technique has been modified to minimize supercooling. Greater than 20 mole % solubility is indicated for UCl_4 in $PbCl_2$ at 380°C.

2. *Stainless-steel Fuel Elements.* Stainless-steel-containing fuel elements may be dissolved in dilute aqua regia (Darex) and in dilute sulfuric acid (Sulfex). The three-step Darex process in-

volves dissolution in dilute nitric–hydrochloric acid, chloride removal, and feed adjustment for solvent extraction.

A single ORNL dissolution run of mixed oxide core materials (16 Davison 93.5 per cent thoria–6.5 per cent urania hydrogen-fired pellets having 93 per cent density) indicated that the core material from one Consolidated Edison assembly could be dissolved in 20 to 24 hr by using as dissolvent an adjusted Darex cladding solution (~10*M* nitric acid, 53 g of stainless steel per liter, 0.04*M* sodium fluoride, less than 350 ppm chloride).[5]

Passivation of type 304 stainless steel in contact with titanium can occur in boiling 5*M* nitric acid–2*M* hydrochloric acid, the usual Darex dissolvent.[5] Increasing the hydrochloric acid concentration to 6*M* reduced the time required for depassivation to essentially zero. Passivation was not encountered with brazed specimens or when the dissolvent contained 0.04*M* sodium fluoride. Continued exposure of titanium to various Darex-Thorex environments indicated the feasibility of using titanium equipment under all conditions envisioned, including environments containing unstripped chloride and stainless steel plus 0.04*M* F^-. Rates in all environments except the initial Thorex solutions containing no Al^{+3} were less than 1 mil/month. In a few cases pitting was observed, but the observed rate of pitting attack was only about 1.4 mils/month.

Simulated Consolidated Edison fuel pins, 95 per cent thoria–5 per cent natural uranium (83 per cent of theoretical density), were irradiated to ~200 Mwd per ton of thorium, and the stainless-steel cladding was dissolved in boiling 5*M* nitric acid–2*M* hydrochloric acid.[11] From intact pellets the uranium losses were ~0.2 per cent in the 30 to 45 min required for cladding dissolution, increasing twofold in an additional 3 hr. From fragmented pellets the uranium, thorium, plutonium, gross beta, and gross gamma losses were 4.9, 5.1, 14, 15, and 3.0 per cent, respectively, in 40 min, increasing to 9.0, 8.2, 23.7, 39.8, and 14.9 per cent in an additional 3 hr. The off-gas caustic scrubber solution trapped 0.04 and 0.15 per cent of the gross beta and gamma activity.

In laboratory-scale dissolutions[11] of unirradiated high-density (94 per cent of theoretical) 4.2 per cent $UO_{2.38}$–95.8 per cent thoria pellets in 200 per cent excess of nitric acid containing 0.04*M* sodium fluoride and 0.1*M* aluminum nitrate, the initial dissolution rate increased from 3.5 to 7 mg/(min)(cm^2) as the acid concentration was increased from 9*M* to 13*M*. The rates were about 20 per cent higher with 400 per cent excess acid. The initial dissolution rate of pellets containing about 4 per cent $UO_{2.03}$ (84 per cent of theoretical density) decreased from 3 to 1.2 mg/(min)(cm^2) as the aluminum concentration in 200 per cent excess of boiling 13*M* nitric acid–0.04*M* sodium fluoride was increased from 0*M* to 0.2*M*. In a small-scale engineering study of a flooded-pot dissolver, where the product is continuously recycled from a holdup vessel to the fresh dissolvent, 90 per cent of the pellets dissolved in 8 hr in 200 per cent excess of 13*M* nitric acid–0.04*M* F^-–0.1*M* Al^{+3}. The dissolution rate was 2.5 mg/(min)(cm^2) based on the initial pellet surface area. For >99.9 per cent dissolution, an additional 26.5 hr was required and two additional charges of acid were required. The average reaction rate was 0.33 mg/(min)(cm^2).

Dissolution of Dejacketed Material

Dissolution of the core is possible if fuel jackets can be removed mechanically or chemically, or it may be performed when the fuel is sheared into pieces. Thus a simpler dissolution procedure may be possible than when combined jacket-core dissolution is carried out.

Studies of the dissolution of uranium-molybdenum alloy fuel cores are being made at HAPO.[2] The Piqua reactor fuel will consist of uranium–3.5 wt.% molybdenum–0.1 wt.% aluminum alloy cores clad in aluminum. Silicon may be substituted for aluminum in the cores. Studies with uranium–3 wt.% molybdenum–0.2 wt.% aluminum and uranium–3 wt.% molybdenum–0.2 wt.% silicon alloys show that the nitric acid–Fe(III) nitrate core dissolving and feed preparation procedures already established for uranium–3 wt.% molybdenum alloy apply equally well to cores containing these amounts of aluminum or silicon.[2]

Various cations and anions were tested at HAPO[3] for their ability to complex molybdate ion formed during nitric acid dissolution of uranium–3 wt.% molybdenum–0.2 wt.% aluminum alloy (uncomplexed molybdate ion forms a white solid during such dissolutions). None of the other cations tested—Mn(II), Cr(III), Ni(II), and Co(II)—appeared to complex molybdate ion to any extent. Phosphate ion at 0.05*M* to 0.2*M*

was found, as expected, to be effective in complexing molybdate ion.

Flow sheets are being developed at ORNL[5] for the dissolution of uranium-molybdenum alloy fuels containing up to 10 per cent molybdenum. The method preferred at present is dissolution in boiling 11*M* nitric acid and separation of the precipitated molybdic acid by centrifugation. About 95 per cent of the molybdenum is thus removed prior to solvent extraction. For fuels containing about 3 per cent molybdenum, a raw solvent-extraction feed solution containing 1*M* uranium was obtained by dissolution in boiling 8*M* nitric acid–0.5*M* $Fe(NO_3)_3$. The molybdenum was solubilized by heteropolymolybdate complex ion formation. This would result in relatively large volumes of high-level radioactive waste.

Studies are being made at ORNL of recovery of uranium and thorium from graphite fuels.[5] Leaching (with 15.8*M* nitric acid) of bromine-treated samples of three graphitized fuels (0.7 per cent uranium-graphite; 2 per cent uranium-graphite; and 1.5 per cent uranium–7.2 per cent thorium-graphite) recovered 97.2, 99.2, and 99.3 per cent of the uranium, respectively.[5] Leaching of −200-mesh samples which had not been subjected to bromine treatment recovered only 87.3, 99.2, and 93.2 per cent of the uranium from the respective fuels. Thorium losses by either method were about 10 per cent.

There was no significant advantage in grinding the 0.7 per cent uranium fuel any finer than 4 mesh. Leaching of −4 +8 samples of admixture graphitized fuels containing 5 to 14 per cent uranium and less than 0.4 per cent iron recovered 99.8 per cent of the uranium either with or without a bromine pretreatment.[11] In the one fuel studied which contained 0.7 per cent iron, bromine treatment before leaching did not affect the uranium recovery. The bromine pretreatment markedly increased the uranium recovery from fuels containing less than 5 per cent uranium, e.g., from 80 to 97 per cent in the case of 0.7 per cent uranium-graphite fuel. Grinding finer than 4 mesh had little or no effect on the uranium recovery from fuels containing less than 2 per cent uranium when the bromine treatment was used.

Laboratory measurements of rates of dissolution of thorium in mixtures of nitric and hydrofluoric acids show that thorium can be dissolved with practicable time cycles in large-scale processing.[19] The corrosion of stainless steel during the dissolution of thorium is acceptable, except that when the thorium is coated with aluminum-silicon alloy, frequently used as a bonding material for aluminum cans, severe local corrosion of the stainless steel occurs at areas of contact with residual aluminum-silicon. This contact corrosion does not occur when the cans are hot-press-bonded to the thorium without aluminum-silicon.

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Solvent Extraction

Purex Process Improvements and Modifications

The Purex process (TBP in kerosene) was originally developed to recover fertile and fissionable values from irradiated natural uranium. This process, now in use in most recovery plants, has received wide application to the recovery of uranium from ores and will also be used to process spent fuel from a number of the first-generation nonproduction reactors. Studies are in progress to improve the process and to adapt it to the needs of the nonproduction reactors.

Purex processing of uranium-aluminum fuels containing silicon has been complicated by the formation of stable emulsions in pulse columns. It appears that soluble silica slowly converts, in the presence of nitric acid, to a polymerized surface-active species. The polymerized species in the presence of zirconium shows surface-active tendencies in acid-free systems. The over-all picture is further complicated by the formation of a soluble surfactant complex between dibutyl phosphate (DBP), a TBP degradation product, and zirconium. The conditions leading to stable emulsion formation were assessed by observing the coalescence time of representative aliquots of suspect solutions. The results of this study showed: (1) all surfactant materials encountered, with the exception of the zirconium-DBP complex, were markedly reduced in effectiveness by the addition of 1*M* nitric acid, and (2) with zirconium present, pronounced surface activity was observed at low acid concentration with little improvement to 1.5*M*. A decrease in surface activity was noted at acid concentrations[1] above 3*M*.

Coalescence time measurements were established as a satisfactory method for predicting major changes in emulsification tendencies in pulse columns. In 88 out of 97 trials in which excessive emulsification was predicted by the coalescence test, the test procedure provided an accurate forecast of column operability.[2]

In conventional Purex processing of irradiated natural uranium, much work has been done at Hanford to determine the effect on column variables of changes in sieve-plate cartridges (column internals). A review of some of the work on column dispersion and coalescence has recently appeared.[3] Under certain conditions a mixed cartridge of linear polyethylene and stainless-steel sieve plates was found to give improved extraction efficiency. The improvement was thought to be associated with the effect that wetting characteristics had on the coalescence and redispersion of the liquid phases. Tests were conducted under both organic-continuous and aqueous-continuous operation with uranium-bearing and uranium-free systems. With a mixed cartridge a mode of column performance, designated the Zebra formation, is observed. The Zebra formation consists of aqueous-continuous operation in the zone of stainless-steel sieve plates and organic-continuous operation in the zone of polyethylene sieve plates and gives, under some conditions, the highest extraction efficiency. The ease of Zebra formation varies. High rates of mass transfer appear to impede Zebra formation, whereas high flow rates aid its formation. Pulse frequency has no effect.[3]

The problem of reducing the volume of aqueous waste produced in the Purex processing of zirconium-clad and/or alloy fuel by extracting zirconium with TBP is being studied.[4] In laboratory tests with synthetic solutions, zirconium was efficiently extracted with TBP from nitric acid solutions of 6*M* and greater provided that the initial fluoride-to-zirconium ratio was less[4] than 1.4. Fluoride is extracted along with zirconium into TBP as $ZrF(NO_3)_3$.

Studies of Alternate Extractants

A number of organonitrogen and organophosphorus compounds have been found to exhibit greater extraction power, selectivity, and versatility than the Purex extractant TBP. Processes utilizing these extractants are in use in the recovery of uranium from ore. A number of

schemes for the application of these extractants to the processing of irradiated fuels are being studied.

Recent studies[5] have shown that, in the presence of aluminum nitrate, Pu(III) can be coextracted with Np(IV) from nitrate solutions by tertiary amines. Without the salting agent, Pu(III) is extracted poorly by all classes of amines. The extraction mechanism is apparently complex because, in stripping tests with 2*M* nitric acid, which would be expected to remove quantitatively Pu(III), over 90 per cent of the plutonium remained in the extractant. The dramatic effect of the aluminum nitrate salting agent is apparent from the data of Table IV-1.

Table IV-1 Pu(III) EXTRACTION WITH 0.1*M* TRIISOOCTYL AMINE IN XYLENE[5]

Nitric acid, *M*	Distribution coefficient, E_a^o	
	Nitric acid alone	6*N* aluminum nitrate plus nitric acid
0.05	3×10^{-5}	170
0.1	7×10^{-5}	300
0.2	4×10^{-4}	
0.3	4×10^{-5}	15

The efficacy of various salting agents in promoting the extraction of rare earths from nitric acid solution by organophosphorus reagents was determined.[5] In the extraction of europium, diamylamyl phosphonate and dibutylbutyl phosphonate (DBBP) were the most powerful extractants, with extraction coefficients an order of magnitude greater than those obtained with TBP. The effect of the salting agent on the TBP distribution coefficient is shown in Table IV-2.

Table IV-2 EFFECT OF SALTING AGENT ON EUROPIUM EXTRACTION WITH 1*M* TBP IN KEROSENE[5]

Salt (5.6*N*)	Distribution coefficient, E_a^o		
	No HNO_3	0.01*M* HNO_3	0.1*M* HNO_3
$Al(NO_3)_3$	270	160	45
$Mg(NO_3)_2$	250	200	40
$Zn(NO_3)_2$	150	130	40
$LiNO_3$	140	160	130
$Cu(NO_3)_2$	60	70	25
$NaNO_3$	9	8	2.9
$Fe(NO_3)_3$	9	9	6
$Ca(NO_3)_2$	9	4	2.5
NH_4NO_3	2.0	1.8	0.9

Laboratory experiments established that strontium could be extracted with di-2-ethylhexyl phosphoric acid (D2EHPA) from caustic-neutralized simulated Purex aqueous waste. However, in studies under process conditions, it was found that ferric ion, present in Purex waste to about 0.5*M*, precipitated as the hydroxide interfering with the D2EHPA extraction. A satisfactory solution to this problem was obtained by adding 1*M* tartrate ion to the waste before neutralization. The tartrate ion complexed the iron and retained it in solution. On subsequent extraction with D2EHPA, iron tended to coextract with strontium. However, good separation of iron and strontium could be effected inasmuch as the strontium-to-iron separation factor varied from 13 to 121 as the phase contact time was decreased from 20 min to 1 min.[5]

A topical report has been issued[6] which discusses several methods being considered for the recovery of uranium from Sulfex decladding solution produced in the dissolution of stainless-steel-clad fuels. The solution is 2*M* to 3*M* in sulfuric acid, 1*M* in stainless-steel metal sulfates, and about 0.01*M* in uranium (the latter representing about a 1 per cent loss). Flow sheets were tested experimentally using a synthetic decladding solution and primary amine, secondary amine, dialkyl phosphoric acid, and trialkyl phosphine oxide. With a primary amine, Primene JM, 0.1*M* to 0.3*M* in a hydrocarbon alcohol diluent, U(IV) and Pu(III) or Pu(IV) were extracted consecutively from a solution treated with chromous ion to maintain U(IV). After uranium was extracted, ferric ion was added to create conditions favorable for plutonium extraction. For the recovery of uranium alone, D2EHPA provided a satisfactory extractant. A synergistic effect was noted on the addition of a small amount of neutral reagent such as TBP, phosphonate, or a phosphine oxide. Thorium was not extracted by the dialkyl phosphoric acid but was extracted with U(IV) by the primary amine.[6]

Further evidence of the versatility of D2EHPA was provided by a bench-scale demonstration of vanadium extraction from ore acid leach liquor. In these studies the extractant was diluted with kerosene to which was added a diluent modifier, TBP or capryl alcohol, to increase the solubility of the extracted complex ion in the solvent. Vanadium and uranium were extracted simultaneously and separated by selective stripping. Vanadium was stripped with dilute sulfuric acid and uranium with 0.94*M* sodium carbonate. V(IV) was extracted more strongly than V(V) with a maximum vanadium loading of 0.5 mole

per mole of D2EHPA. The diluent modifiers depressed the vanadium extraction coefficient, but TBP exerted a synergistic effect on uranium extraction. In seven experiments vanadium recoveries were 82 to 93 per cent, and uranium recoveries were better than 99 per cent.[7]

Solvent Degradation

Although for the present most of the fuel from the first-generation power reactors is scheduled to be processed at Hanford via the Redox (hexone) process, for future planning as well as the processing of the fuels presently scheduled for the other sites Purex type processes are expected to be used. The high burn-up of these fuels presents radiation levels not previously encountered, and, accordingly, increased efforts have been applied to the study of radiation damage to process solvents and diluents. Certain of the degradation products of the TBP form strong complexes in the organic phase with uranium and various fission products. The limits of Purex processing are apparently being closely approached, and considerable activity is evident in the study of the radiation resistance of alternate extractants.

The most objectionable TBP degradation product is DBP. It forms complexes with uranium and zirconium which strongly favor the organic phase. Studies are in progress[8,9] to determine the properties of zirconium-DBP in Purex solutions by means of a Zr^{95} tracer technique. In aqueous uranyl nitrate–nitric acid solutions, the solubility of zirconium-DBP varied from 0.35 to 159 mg of zirconium per liter. In contrast, in 30 per cent TBP in kerosene solutions equilibrated with aqueous uranyl nitrate–nitric acid solutions, the solubility of zirconium-DBP varied from 330 to 3550 mg of zirconium per liter. The highest solubilities were associated with systems typical of stripping operations; namely, low acid (0.04*M*) and relatively high uranium (110 g/liter) concentrations. These concentrations of zirconium are in excess of those encountered in the Purex processing of irradiated natural uranium.

Removal of complexed uranium and fission-product activity from used Purex solvent is necessary before recycle. The conventional procedure is to scrub the used solvent with an aqueous solution of sodium carbonate. Some recent findings indicate that a prior scrub with sulfuric acid may be beneficial in that it provides a favorable uranium distribution coefficient. In tests with Purex solvent used in ore refining, the uranium concentration was reduced from 0.3 to 0.01 g/liter by sulfuric acid washing. However, the effectiveness of sulfuric acid washing was decreased by the presence of small amounts of nitrate ion. This presents a serious limitation to potential applications of the technique.[10]

Further studies on the resistance of various extractants to radiation-induced decomposition at high levels of irradiation continue to demonstrate the higher level of stability, as compared to TBP, of some of the organophosphorus compounds of recent interest.[11] In Table IV-3, TBP, di-*sec*-butylphenyl phosphonate (D-*s*-BPP), and di-*n*-butylphenyl phosphonate (D-*n*-BPP) are compared with respect to acid and gas yields.

Table IV-3 COMPARISON OF RADIOLYTIC DECOMPOSITION[11] OF D-*n*-BPP, D-*s*-BPP, AND TBP

	D-*n*-BPP		D-*s*-BPP		TBP
	Pure* at a dose of 400 watt-hr/liter	1*M*† at a dose of 210 watt-hr/liter	Pure* at a dose of 200 watt-hr/liter	1*M*† at a dose of 200 watt-hr/liter	Pure* at a dose of 300 watt-hr/liter
Monobasic acid, g	0.78	0.22	0.54	0.26	2.07
Gas, g	0.49	1.67	0.33	1.01	1.87

*Indicated compound used as extractant without dilution.
†Indicated compound diluted with 20 per cent xylene in kerosene before use as extractant.

Fundamental Solvent-extraction Studies

The findings of another study of the kinetics and mechanism of uranium transfer under Purex conditions have been published.[12] Equilibrium data were obtained by means of a U^{233} tracer technique. The experimental apparatus

features an hourglass-shaped container with a small undisturbed interphase area. Mixing of the bulk phases eliminated any rate-controlling effect ascribable to molecular diffusion. The mechanism of chemical reaction was postulated as the generally accepted series of reactions in which the uranyl nitrate ion ultimately forms a complex with 2 moles of TBP. However, the rate measurements covering the temperature range to 45°C indicated a probable change in the mechanism with temperature. The rate of transfer (moles per square centimeter per second) at 25°C was expressed by the following equation:

$$\text{Rate} = k(UO_2^{++})_{aq}\ (NO_3^-)_{aq}^{1.2}\ (TBP)_{org}^{1.8}$$

At 25°C the rate constant k was 2.2×10^{-4}.

It has long been recognized that decontamination in Purex processes was quite sensitive to the degree of uranium saturation of the solvent. This effect is explained quite simply. Uranium with its high distribution coefficient (higher than that of any other species encountered in most separations problems) can conceivably complex all available TBP molecules. In a precise experimental evaluation of the uranium saturation effect on decontamination from nitric acid, thorium, europium, and zirconium, factors which improved with increasing uranium concentration were noted for all species except zirconium. In the case of zirconium at lower nitric acid concentrations (~1*M*), the distribution coefficient actually reached a maximum at 50 per cent uranium saturation, increasing by a factor of 3 as the uranium saturation increased from 0 to 50 per cent. By comparison the distribution coefficients for europium in 1*M* nitric acid and 2*M* nitric acid decreased by factors of 1000 at 80 per cent uranium saturation and 100 at 90 per cent uranium saturation, respectively.[13]

Third-phase formation in amine systems is attributable to the low solubility of the extracted complex and thus is highly sensitive to the choice of diluent. In contact with mineral acids, the susceptibility of amines to third-phase formation increased in the order nitric acid, sulfuric acid, hydrochloric acid. Increasing the temperature from 25 to 50°C reduced the tendency toward third-phase formation. Toluene and xylene were better diluents than kerosene or Decalin. In the case of the latter two, improved solubility of the extracted complex was noted on addition of 5 to 10 per cent of a long chain alcohol.[14]

By use of a P^{32}-labeled TBP tracer technique, it was shown that the solubility of TBP degradation products in thorium product was 7×10^{-5} mole/liter. Complete stripping of thorium with water removed 1 per cent of the degradation products from the solvent. Three treatments of the thorium-free solvent with 0.2*M* sodium carbonate followed by filtration removed 93 per cent of the degradation products. A variety of other treatments were studied. The most important conclusion to be drawn from this work is that the full efficacy of alkaline scrubbing of degraded solvent can only be realized by a subsequent filtration to remove the precipitate. Contacting the treated solvent with acid solution will result in the redissolution of any precipitate present.[15]

Precipitation Processes

The first large-scale processing of aluminum alloy reactor fuel containing significant amounts of aluminum-silicon bonding agent has been carried out at the ICPP. The fuel tubes are so fabricated that about 8 in. of the core at each end is aluminum alloy containing 7.5 per cent silicon. The central portion of the core is uranium-aluminum alloy. Cladding is aluminum metal containing 0.1 to 0.3 per cent silicon. Silicon from the end portions of the core is insoluble in nitric acid and appears in the dissolver solution as elemental silicon.

In the first prolonged processing of this type of fuel, an unexpected amount of difficulty was encountered centering around extraction column interfaces and pump check valves where solid particles can cause trouble. It was decided, therefore, to cut off and separately process the end sections which contain all of the aluminum-silicon alloy. The end pieces were dissolved batchwise in mercury-catalyzed nitric acid, and the undissolved silicon was filtered off. Results of laboratory experiments and pilot-plant filtration tests on simulated end-piece solutions have recently been reported.[16,17]

Acidic solutions treated by the addition of about 120 mg of gelatin per liter and digested at about 90°C for 1 hr gave clear filtrates at a rate of about 43 liters per hour per square foot of filtering area through a 20-μ sintered stainless-steel star filter. Filtration rates for

a 5-μ filter were about one-half as large. Both filtrates had coalescence times with TBP solvent which are acceptable in the extraction columns. Filtration without gelatin resulted in rapid plugging of the filter. The use of a 15-μ wire-screen filter gave no apparent filtration.

Water washing removed nearly all the uranium in the filter cake. Backwashing with steam followed by water gave flow rates comparable with those for a new filter. The 20-μ filters were recommended for plant use.

Ion-exchange Processes

Processes involving ion exchange have been applied to recovery and purification of uranium, plutonium, neptunium, and other elements from process solutions.

Ion-exchange Processes for Recovery and Purification of Uranium

Previous Reviews[18–21] have discussed recovery and purification of uranium by ion exchange.

The unit operation of semicontinuous ion exchange has been applied to the recovery of uranium from tonnage quantities of metal reduction residues and other solid salvage materials.[22] This method, a departure from nitric acid and solvent-extraction techniques, was chosen to take advantage of elimination of costly complexing agents, adaptability of the ion-exchange processes to unclarified feed solutions, and the suitability of the column contactor design to specific limitations of nuclearly safe process geometry. The operation involves the roasting and size reduction of the solid gangue material prior to sulfuric acid digestion under controlled conditions of *p*H, temperature, and oxidation potential. The resulting uranyl sulfate slurry is partially clarified to 2 to 10 vol.% solids using conventional process equipment and is pumped to the contactor. The uranium is adsorbed on strongly basic anion-exchange resins (such as F7L resin) as an anionic uranyl sulfate complex and is recovered in purified and concentrated form by elution with an acidified ammonium nitrate solution. The product is precipitated with ammonium hydroxide, and the resulting ammonium diuranate cake is calcined to U_3O_8.

Fixed-bed ion exchange and amine complexant solvent extraction have been studied at ORNL as a method to recover uranium from Chattanooga-shale leach solutions. Experimental work has indicated that both of these processes will operate satisfactorily. Two reports discuss the costs of ion exchange and solvent extraction.[23,24] The costs of the two methods are compared in Table IV-4.

Table IV-4 COMPARISON OF COST ESTIMATES FOR SOLVENT-EXTRACTION AND ION-EXCHANGE[24] PROCESSING OF CHATTANOOGA-SHALE LEACH SOLUTIONS

Leach liquor*	Complexant†	Unit cost, dollars per pound	Capital required, millions of dollars
	Solvent Extraction		
CCD	S-24	0.95	1.18
OPL	S-24	1.10	1.34
OPL	NBA	1.10	1.15
	Ion Exchange		
CCD	XE123	1.64	2.31
OPL	XE123	17.55	7.25

*CCD = countercurrent leach, OPL = oxygen pressure leach.

†S-24 = special amine; NBA = *n*-benzylamine; XE123 = resin manufactured by Rohm and Haas.

Separation and Purification of Neptunium by Ion Exchange

The purification and concentration of plutonium by anion exchange in nitric acid have been exhaustively studied,[20,25–27] and the potential of anion exchange in nitric acid for decontamination of plutonium from fission products, uranium, and metallic impurities has been adequately demonstrated.[19] Because of this background and because of the similarity in chemistry of Pu(IV) and Np(IV), only limited investigations have been carried out on the anion-exchange behavior of Np(IV) in nitric acid. These investigations have indicated the feasibility of anion-exchange adsorption of Np(IV) from nitric acid solution and have shown that its anion-exchange properties are very similar in most respects to those of plutonium.

In work at Harwell[28] the process of reducing Np(V) to Np(IV) and Pu(IV) to Pu(III) by ammonium iodide in concentrated hydrochloric acid and passing the solution through an anion-exchange resin (Deacidite FF) gives a very efficient separation of neptunium and plutonium

with 100 per cent recovery of the latter. The elution of neptunium with 2*M* hydrochloric acid gives an excellent recovery without the necessity of using large volumes of elutrient as is necessary in a nitric acid system.

Two methods are presented by Roberts and Bauer[29] by which trace amounts of several actinide elements are separated. Use is made of the large differences in distribution coefficients; thus careful chromotographic techniques are not necessary. Small columns are used, allowing the desired constituent to be obtained in 10 mm or less. The first method separates americium, plutonium, and neptunium. These elements are sequentially eluted from columns of Dowex resin in that order by 8*M* nitric acid, 0.02*M* ferrous sulfamate in 4.5*M* nitric acid, and 0.001*M* ceric sulfate in 0.25*M* nitric acid. In the second method americium, thorium, plutonium, and neptunium are sequentially eluted in that order by 8*M* nitric acid, 12*M* hydrochloric acid–0.1*M* ammonium iodide, and 4*M* hydrochloric acid. Protactinium and uranium follow the americium in both methods. The methods presented are characterized by a low degree of cross contamination. Yields are greater than 95 per cent.

Miscellaneous Ion-exchange Studies

Many of the transuranium elements readily form stable anionic complexes in strong nitric acid solutions. This characteristic, coupled with the high selectivity of anion-exchange resins, has made their use for the recovery of these elements very attractive. A program was initiated to study the operating characteristics of a fixed-bed anion-exchange column.[30] A typical feed stream was used containing 7*M* nitric acid and sufficient ferrous sulfamate for valence adjustment.

Ion-exchange equipment design is complicated by several factors, two of which are (1) limitation on column geometry because of criticality considerations and (2) the formation in the resin bed of product gases of the reaction between the ferrous sulfamate and nitric acid. Criticality considerations require the use of restricted geometries, such as slab or annular columns, to permit operation at high rates without column pressurization. Gas formation in the resin bed is expected to produce fluid channeling and bed loading problems. The purpose of these studies was to investigate the effect of gas formation on the operating characteristics and efficiency of both simple and annular fixed-bed resin columns.

Items investigated included pressure drop, resin fluidization, fluid channeling, and resin-bed loading in the presence and absence of ferrous sulfamate–nitric acid reaction-produced gas in the bed. Studies were made in a simple 6-in.-ID annular column. The significant findings are listed below:

1. The pressure drop through the annular bed was increased by a factor of 2 by the formation of gas.
2. Complete removal of the resin bed by fluidization would be difficult, especially from an annular column.
3. Considerably higher upflow rates were required for particle classification in an annular column than in a simple column owing to the excessive fluid channeling encountered with upflow through an annular bed.
4. The presence of gas in either column reduced the throughput capacity at a 10 per cent breakthrough ($C/C_0 = 0.1$) approximately 30 per cent.

Dowex-50W-X12 resin that had received a total beta-radiation dose of 11.9 watt-hr per dry gram during the processing of Pm^{147} was examined for radiation damage.[31] Its color had changed from light yellow to dark red; its total ion-exchange capacity had decreased from 4.10 to 3.67 milliequivalents per dry gram; and its moisture content had increased from 43 to 72 per cent. The change in moisture content corresponds to a change in cross-linking from 12 to 4 per cent, neglecting the effect of change in capacity at the same time.

The separation of cerium and thorium ions was studied[32] with a lead-EDTA complex solution as eluant. The optimum conditions were determined as the following: the concentration of the lead-EDTA solution was 0.015 mole, the *p*H was 3.0, and the flow rate was 1.0 to 1.5 ml/min. Thorium ions were completely eluted with 200 ml of the eluant at the optimum conditions, whereas no cerium ions were detected in the effluent with 1000 ml of the eluant. Thus the use of a lead-EDTA complex solution as eluant was concluded to be effective for separation of cerium and thorium ions.

Studies at Hanford[33–35] are concerned with development of a Jiggler contactor. Shakedown runs have been started on the initial pilot jigged-

bed continuous countercurrent ion-exchange contactor. A qualitative demonstration run indicates a probability that a nonpulsed, nonfixed packed-bed elution column may be paired with the jigged-bed adsorber for continuous recycling of ion-exchange resin.[35] A simulated feed of 7*M* nitric acid was pumped through the adsorption section at 160 gal/(hr)(sq ft). Resin, with some feed, was moved from the bottom of the latter to the packed bed by pulsation. Resin from the elution section was returned by gravity flow to the top of the adsorption column. The ability of the Jiggler contactor to recycle 7*M* nitric acid and resin at a net feed rate of 160 gal/(hr)(sq ft) has been demonstrated[19] using a pulse frequency and amplitude of $6\frac{1}{2}$ cycles/min and $1\frac{5}{8}$ in., respectively. Under these conditions a resin flow of 20 gal/(hr)(sq ft) and a slip water-to-resin flow ratio of 6.3 was maintained.

A new mechanical pulse generator has been installed on the 3-in.-diameter Weiss type contactor,[34] permitting operation at amplitudes up to 0.8 in. and frequencies up to 200 cycles/min. Results indicate stable operation and uniform resin transfer at fluid flow rates up to 100 gal/(hr)(sq ft) and resin flow rates up to 70 gal/(hr)(sq ft) (wet settled basis). [A fluid flow rate of 100 gal/(hr)(sq ft) is not sufficient for most plutonium-adsorption column applications but is ample for the elution column.] Operation at amplitudes of 0.125 to 0.25 in. and frequencies greater than 150 cycles/min result in a semi-fluidized bed of resin on each support plate. Fluid channeling under these conditions should not be excessive.

Volatility Processes

The volatility of uranium hexafluoride is used as a basis for several schemes for processing irradiated fuels. Progress is reported on three such schemes: the fused-fluoride volatility process, the aqueous dissolution fluorination (ADF) process, and a direct fluorination process. The latter two make extensive use of fluidization techniques.

ADF Process: Application of Uranium-Zirconium Alloy Fuels

Laboratory and pilot-plant scale development of a fluid-bed volatility process for the recovery of uranium from low-uranium–Zircaloy-2 fuel alloys was continued at Argonne National Laboratory (ANL).[36] This process involves aqueous dissolution of the fuel, fluid-bed drying of the solution to a dry fluidizable powder, and fluid-bed fluorination of the material, to remove and recover the uranium as the volatile uranium hexafluoride. Very reliable operation of the 6-in.-diameter fluid-bed dryer was achieved in runs of 36 and 54 hr using a newly designed spray nozzle (Fig. 7). Synthetic feed solutions

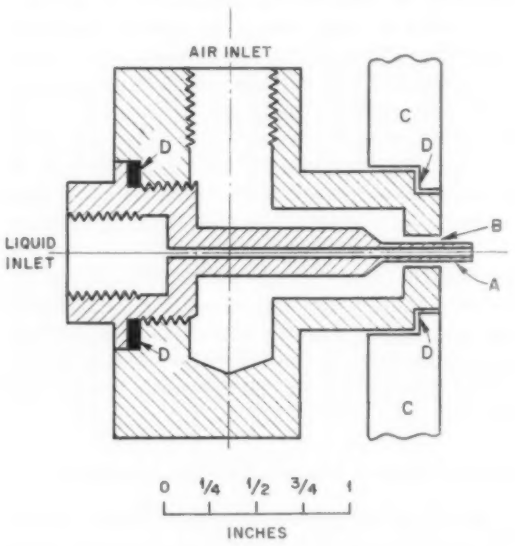

Figure 7 — Two-fluid spray nozzle.[36] *A*, liquid nozzle. *B*, air annulus. *C*, column wall. *D*, gasket.

containing the equivalent of a 2 wt.% uranium alloy and a high fluoride content (~14*M*) were fed at rates up to 140 ml/min (for 18-in. bed height). Runs made at temperatures of 240, 300, and 350 produced 4.4 lb/hr of dry zirconium-uranium fluoride powder. The use of a high-velocity air jet and an oversize air annulus on the atomizing side of the feed nozzle limited particle growth during calciner operation by promoting particle attrition.

Stable zirconium fluoride feed solutions of a concentration higher than heretofore thought possible (>3.5*M* zirconium) have been prepared from the dissolution of both zirconium metal turnings and zirconium tetrafluoride in aqueous hydrofluoric acid. The composition corresponds to 30 per cent hydrogen fluoride, 30 per cent zirconium oxide, and 40 per cent water.

A statistical experiment to study the factors affecting uranium removal from the zirconium fluoride matrix during fluid-bed fluorination was completed. Evaluation of the data indicates reaction temperature is the most significant variable. Factors such as pretreatments (hydrofluorination or low-temperature fluorination), particle size, or water and oxygen content of the zirconium fluoride matrix had only moderate effect on uranium removal.

Further laboratory-scale studies on the fluorination of fluid-bed dried solids of high zirconium concentration indicated that temperatures in excess of 600°C are needed for complete uranium removal in less than 30 min. Pretreatment of the solids with hydrogen fluoride prior to fluorination had a negative effect on the removal of uranium. Grinding of the solids by "ball milling" had an enhanced effect on the removal of uranium from some of the samples and little effect on others.

Static corrosion experiments conducted in fluorine at 675°C in the presence of nonfluidized zirconium tetrafluoride indicate that Monel is severely attacked dimensionally, whereas "A" nickel shows greater resistance to dimensional attack. Monel showed essentially no intergranular attack. Tests on recrystallized alumina at 650°C showed no dimensional changes, but some weight gains were noted. Data are presented in Table IV-5.

Table IV-5 SUMMARY OF STATIC CORROSION EXPERIMENTS IN FIXED BEDS OF ZIRCONIUM TETRAFLUORIDE IN A FLUORINE ATMOSPHERE[36]

Material	Bed	Exposure time, hr	Treated fluorine*	Max. bed temp., °C	Max. dimensional change, mils	Intergranular attack, mils	
						Typical	Maximum
Nickel†	None	70	Yes	600	0.1	0.4	0.5
Nickel†	ZrF_4	70	No	600	1.5	2.7	5.9
Nickel†	ZrF_4 + 5% AlF_3	28	No	600	0.1	1.2	1.6
Monel	ZrF_4	70	No	675	>62‡	0	0
Monel	ZrF_4	49	Yes	675	>62‡	0	0
Nickel†	ZrF_4	70	No	675	4.4	5.6	5.9
Nickel†	ZrF_4	70	Yes	675	4.0	5.7	7.0
Recrystallized Al_2O_3	ZrF_4	7	No	650	0		

*Fluorine is treated by passing it through a bed of porous sodium fluoride.
†Nickel was "A" nickel, fine-grained and annealed.
‡Metal perforated through wall.

Direct Fluorination Process: Application to Uranium Oxide and Plutonium Oxide Fuels

A process is being developed at ANL for the direct fluorination of ceramic fuels containing uranium oxide.[36] Fluorination rate data on uranium dioxide have been reported previously.[18,21] The conversion of plutonium tetrafluoride and plutonium dioxide to the hexafluoride by elemental fluorine was investigated on a laboratory scale in a flow system at temperatures[37] between 100 and 600°C. The partial pressure of fluorine used was varied from 0.25 to 1.0 atm. The rates of fluorination were dependent on the source of the starting material, probably due to differences in specific surface area. The activation energies of the reaction were between 10 and 12 kcal/mole. The rate data indicate that both plutonium tetrafluoride and plutonium dioxide can be fluorinated in simple equipment under moderate conditions at sufficiently high rates for process use.

Additional values of the equilibrium constant have been obtained for the reaction

$$PuF_4(s) + F_2(g) \rightleftharpoons PuF_6(g)$$

at 200, 250, and 350°C. Data are given in Table IV-6.

The vapor pressures of the hexafluorides of plutonium and neptunium have been determined,

and the thermodynamic properties have been compared with those of uranium hexafluoride.[38] (The vapor pressures were presented in a previous issue of this Review.[18]) A literature survey of the properties of fission-element oxides, fluorides, and oxyfluorides has been made.[39]

Fused-salt Volatility Processes

Development of fluorination processes employing fused-fluoride media have continued. The chief applications have been to zirconium-uranium alloy reactor fuels and to the fluid fuel of the molten-salt reactor (ORNL). A major development problem has been corrosion in both the hydrofluorination and fluorination steps. Use of special nickel alloys, graphite, and frozen-salt protection of vessel walls has been under development.

In continuing studies of the fused-fluoride volatility process at ANL, three zirconium dummy fuel elements were dissolved in the pilot-plant graphite dissolver.[36] The dissolutions were carried out at 600°C, and they showed a dissolution rate increasing with sparge rate. At the highest sparge rate used (30 lb of HF per hour), the dissolution rate was 4.1 mils/hr or 1.1 mg/(cm^2)(min). No difficulties with the heaters or other graphite components appeared during these operations, in which the dissolver was held at temperature continuously for a period of about three weeks.

A preliminary test of an electrolytically heated frozen-wall fluorinator was carried out.[40] This unit is shown schematically in Fig. 8. Power is brought into the bottom of the electrodes to minimize the shorting out effect of salt at the surface and thereby allow heat to be introduced more uniformly throughout the salt volume. Thermowells, a sparge line, and resistance heaters for start-up are also contained in the well of each heater. A 38-in.-deep 17-in.-diameter batch of salt was initially melted with resistance heaters contained in the electrodes, and the salt was held molten by electrolytic heating for over a week with forced cooling of the wall to provide a protective layer of solid salt. The frozen-salt wall thickness measured between 1 and 1.5 in. over nearly 80 per cent of the liquid depth. The salt thickness was 5 in. at the bottom in these tests. Electric power to the heaters was controlled automatically by measurement of the resistance of the frozen wall.

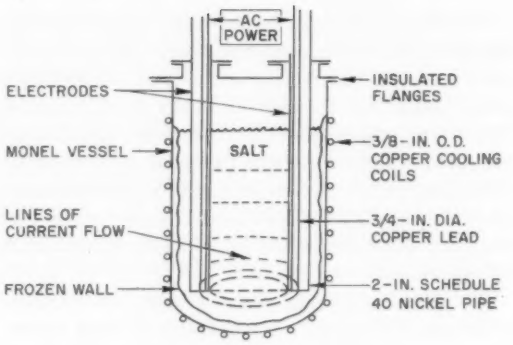

Figure 8 — Electrolytically heated frozen-wall fluorinator.[40]

Table IV-6 EQUILIBRIUM CONSTANTS FOR THE REACTION[38] $PuF_4(s) + F_2(g) \rightleftharpoons PuF_6(g)$

No.	Total pressure at equilibrium, mm Hg	Equilibrium temp., °C	Equilibrium constant*
8	6230	199 ± 0.5	0.000708
9	6270	202 ± 0.5	0.000620
12	6250	200 ± 0.5	0.000818
15	6230	200 ± 0.8	0.000667
16	5020	251 ± 0.3	0.00164
17	3690	251 ± 0.5	0.00151
18	3140	342 ± 0.3	0.00380
19	2320	336 ± 0.3	0.00334

*$K_p = K_c = (PuF_6)/(F_2)$.

A review has been presented of a process for recovery of core and blanket materials of the molten-salt power reactor.[41] (A preliminary flow sheet was presented in a previous Review.[21]) This process involves volatilization of uranium hexafluoride with subsequent dissolution of the Li^7F-BeF_2 carrier salt in nearly anhydrous HF.

Miscellaneous

A review of methods for quantitative recovery of uranium hexafluoride from process gas streams has been presented by Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant.[42] Discussion and references mainly from their own development work are cited for cold trapping, liquid condensation, absorption (in an inert liquid) and distillation, and the use of solid adsorbents. Among solid adsorbents, sodium fluoride has been used with success in fixed beds and uranium tetrafluoride in fluid beds.

Where small amounts of uranium hexafluoride are involved and further recovery costs are not considered important, other solid trapping materials have been used: chemical traps of activated carbon or soda lime, and absorbent beds of calcium sulfate, calcium fluoride, and activated alumina. Water scrubbing has been used to produce uranyl fluoride solution; caustic may be used to neutralize hydrofluoric acid in the gas stream. Trichloroethylene reacts with the hexafluoride in the vapor phase to produce uranium tetrafluoride. The vapor-phase reaction of hexafluoride with steam produces uranyl fluoride.

Fluid-bed absorption of uranium hexafluoride into uranium tetrafluoride was described further by Powell et al.[43] at the Paducah Gaseous Diffusion Plant. Initial batch type fluid-bed reactor tests were made in a 2-in. Monel reactor with 24-in.-deep beds. Gaseous mixtures of air, 0 to 3 per cent fluorine, and 0 to 10,000 ppm uranium hexafluoride were fed to the bed at various rates. A temperature of 200°C gave optimum uranium hexafluoride recovery. A gas velocity of 0.4 to 0.5 ft/sec was necessary to fluidize the uranium tetrafluoride. Pressure drop was about 1 psi per foot of fluid bed.

The recovery efficiency for uranium hexafluoride was essentially unaffected by the purity of the green salt; however, fluorine-removal efficiency was enhanced by presence of oxides. Maximum bed loading with pure green salt at 200°C was 0.15 lb of uranium hexafluoride per pound of green salt for uranium hexafluoride in air. With about 3 per cent fluorine present, the loadings were 0.085 and 0.011 for uranium hexafluoride and fluorine, respectively.

The uranium hexafluoride concentration was reduced to less than 10 ppm regardless of concentration so long as the bed was not near exhaustion. This suggests that the outlet concentration is only a function of uranium hexafluoride vapor pressure over the intermediates formed, if the gas has sufficient retention time in the fluidized bed. A plant-scale fluid-bed unit, installed at Paducah in July 1958, handles up to 95 cu ft of vent gas per minute.

Pyrometallurgical Processing

Pyrometallurgical processes are being worked on at several sites in the hope that they will provide a reduction in fuel-processing costs through elimination of chemical conversions and ability to process short-cooled fuel. Information is included in this Review on melt refining, liquid-metal processes, and the application of pyrometallurgical techniques to ceramic fuels.

Melt Refining

A direct-cycle fuel-processing plant incorporating the melt-refining process is now under construction at the National Reactor Testing Station as part of Argonne's Second Experimental Breeder Reactor Project. The recent status of development, design, and construction has been reported.[44] The processing facility, costing about $9 million, is scheduled to be completed around March 1961. Discharged fuel recovered by the melt-refining process will be refabricated into new fuel elements and recycled directly back to the reactor.

A series of five articles[45–49] on development of the melt-refining process for plutonium and uranium alloy fuels has been published. These include articles on process description, experimental furnaces, preparation of alloys, interactions of uranium and its alloys with refractory oxides, and process yields. This information has been covered from time to time in previous Reviews on a progress-report basis.

A bibliography of reports relating to the now discontinued Processing Refabrication Experiment (PRE) for SRE irradiated fuels has been issued.[50]

Liquid Metal and Salt Processes

The chemistry of liquid-metal solvent systems is being studied at several sites to permit design of pyrometallurgical separations processes and to accumulate fundamental data for theoretical correlations. The general processes under consideration consist of dissolution of the fuel material in an appropriate metal solvent, separation of impurity elements including fission products by selective crystallization, and/or extractions into immiscible liquids (fused salts or metals), and recovery of fissile materials by evaporation of the solvent metal. The principal solvent metals being studied are zinc, cadmium, magnesium, mercury, and aluminum.

Important to the design of liquid-metal processing schemes are the solubilities of elements whose separations are being attempted and of structural metals over appropriate temperature and composition ranges. An investigation of the solubilities in cadmium of the first transition

series metals, which are useful construction materials, showed vanadium to be virtually insoluble (less than 0.2 ppm at 650°C), iron to have a low solubility (less than 0.5 ppm at 450°C, increasing to 7 ppm at 610°C), and nickel to be fairly soluble (1.43 per cent at 410°C and 4.9 per cent at 541°C).[44] Nickel was also found to precipitate uranium from cadmium solution. The possibility of leaching nickel from 300-series stainless steel by molten cadmium eliminates the use of this material in many applications. The change of iron solubility with temperature shows the possibility of mass-transfer corrosion. However, the circulation of 15 and 30 per cent magnesium-cadmium alloys in medium carbon steel thermal-convection loops under thermal gradients of 575 to 675°C and 630 to 725°C resulted in maximum metal transfer of only 6 mils in 1000 hr.

Solubility data for several elements in zinc have been fitted to equations of the form: log (at.% solute) = $A + BT$ by the constants shown below:[44]

Solute	Temp. range, °C	A	B	Av. deviation of data from equation, %
Zr	431–545	8.982 ± 0.090	−7525 ± 67	2.1
Zr	545–732	4.255 ± 0.106	−3609 ± 98	5.3
Pd	439–750	4.034 ± 0.052	−3212 ± 43	5.5
Mo	422–450	2.527 ± 0.390	−3587 ± 296	11.4

The solubility data for thorium in zinc may be represented by the equation[44]

$$\log (\text{at.\% thorium}) = 8.025 - \frac{10{,}391}{T} + \frac{1.779 \times 10^6}{T^2}$$

The high-temperature thermal analysis data obtained at Iowa State College also fall along this line.[51]

The solubility of uranium in liquid cadmium is shown in Fig. 9. The peritectic temperature has been determined to be 474 ± 1°C. Above the peritectic temperature the uranium solubility is slightly retrograde.

Thermodynamic data for the liquid-metal systems are also being accumulated. Measurements of the activity coefficients of uranium in molten lead and aluminum have been reported.[44]

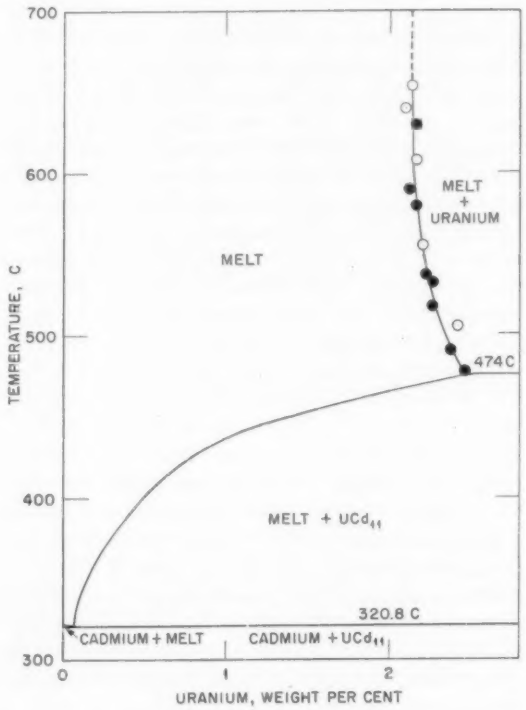

Figure 9—Cadmium-rich portion of cadmium-uranium phase diagram, showing data taken on retrograde solubility region of liquidus.[44] ○, samples taken on heating. ●, samples taken on cooling.

Some thermodynamic data for uranium- and thorium-zinc compounds have been recently reported by Ames Laboratory.[52]

A liquid-metal process is being developed at ANL for recovery of fissionable material contained in the crucible skull and residue of the melt-refining process. Recent results (not yet reported) have been very encouraging. The skull is removed by oxidation to a powder which is subsequently reduced by magnesium in a zinc or cadmium solution. Uranium is precipitated and, after removal of the supernatant liquid bearing most of the impurities, is retorted to vaporize residual solvent metals.[36,40,44]

A liquid-metal process employing aluminum as the metal solvent is under development by the Dow Chemical Company. The process involves dissolution of the uranium in aluminum and subsequent precipitation of UAl_3 to effect some separation from fission products. The low volatility of aluminum makes isolation of

uranium by evaporation of the aluminum impractical. Therefore the most natural application of the process is to uranium-aluminum fuels. However, to extend the application of this process to uranium metal fuels, two methods of decomposing the UAl_3 are being investigated.[53–55] One of these involves the addition of excess magnesium up to a 60 : 1, Mg : U weight ratio. It is reported that this decomposes the bulk of the UAl_3, giving uranium metal, although some aluminum remains as UAl_2. The other procedure employs zinc in weight ratios of 15 or 20 to 1 to cause a conversion to U_2Zn_{17}, which is retortable to uranium metal. Graphite is the preferred container material.

In tracer runs, fairly good removal of rare earths, strontium, and yttrium has been realized. Ruthenium removal has been poor, limited apparently by a low solubility of ruthenium in aluminum.

At Ames, study was continued[52] on the two-phase system, zinc and a KCl-LiCl eutectic, in which zinc chloride and magnesium may be used as oxidizing and reducing agents, respectively, to transfer solute elements back and forth between salt and metal phases. The simultaneous distribution of uranium, thorium, and zirconium between salt and metal phases was determined as a function of the amount of oxidizing or reducing agent added to the system. Oxidation of both uranium and thorium was essentially complete before that of zirconium commenced, indicating a possible means of zirconium separation (Fig. 10). Uranium oxidized more easily than thorium, but the oxidation of thorium began before that of uranium was complete. The sequence of reduction was the reverse of that of oxidation (Fig. 11).

In the above system, yttrium and uranium were simultaneously oxidized by zinc chloride into the salt phase. From measurements of the distribution ratios, it was concluded that the activity coefficient of yttrium in zinc is exceedingly small. This is to be expected since the activity coefficient of cerium, a similar metal, has previously been reported[56] to be of the order of 10^{-9}. Extraction studies are also being made on distribution of fission products between a KCl-LiCl eutectic containing up to 15 per cent magnesium chloride and a magnesium–42 per cent thorium alloy. Rare-earth elements distribute preferentially into the salt phase.

Distribution of various fission products between molten magnesium-silver and uranium-

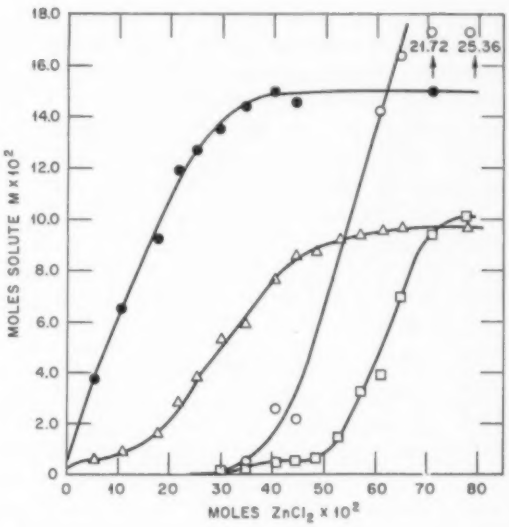

Figure 10—Transfer of solutes (uranium, thorium, and zirconium) from a zinc-rich phase to KCl-LiCl eutectic by oxidation with zinc chloride.[52] ●, uranium. △, thorium. □, zirconium. ○, zinc.

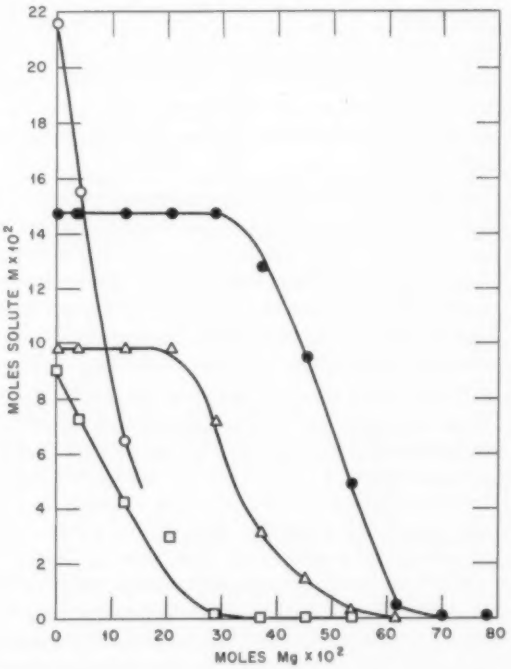

Figure 11—Transfer of solutes (uranium, thorium, and zirconium) from KCl-LiCl eutectic to zinc-rich phase by reduction with magnesium.[52] ●, uranium. △, thorium. □, zirconium. ○, zinc.

chromium alloys is also being investigated at Ames.[52,57,58] Terbium, neodymium, and samarium are essentially quantitatively extracted into the silver-magnesium phase.

In connection with the processing of thorium fuels, thoria reductions by aluminum in the presence of various molten fluoride salts are being investigated by Atomics International. In the presence of cryolite, cryolite–sodium fluoride mixtures, and pure sodium fluoride, reductions of 90 per cent or over were achieved in about 4 hr.[59–61]

The ARCO process (see Sec. III of this Review), under development by Phillips Petroleum at the AEC's National Reactor Testing Station near Idaho Falls, Idaho, consists of dissolution of zirconium-uranium alloys or other active metals such as aluminum in molten lead chloride media. The scale of experimentation has been increased to 100 g of uranium alloy, and three runs have been made with irradiated coupons.[62] The uranium appears almost quantitatively in the salt phase, very little appearing in the lead reaction product or being volatilized. Cesium, strontium, and cerium activities also distribute predominantly into the salt phase, whereas ruthenium favors the lead phase. Two alloys (Incoloy-804 and Carpenter-20) show promise as container materials, having encouragingly low corrosion rates of 3 to 6 mils/month.

Abstract bulletins on liquid-metals technology are being issued quarterly by the MSA Research Corporation, Callery, Pa. These cover current literature on liquid metals and often provide useful information in connection with process applications. The thirteenth of the series was recently issued.[63]

Three electrical methods of heating liquid-metal piping systems (resistance, induction, and transformer heating) are discussed by Baker and Lohman.[64]

Processing of Ceramic Fuels

Work is in progress at several sites on the development of simple recovery processes for highly irradiated short-cooled uranium oxide and other ceramic fuels. Further studies of the "salt-cycle process" under development at Hanford have been reported.[34,35,65] This process involves dissolution of uranium oxide by the action of chlorine to produce UO_2Cl_2 in molten chlorides (generally a eutectic of sodium and potassium chlorides) followed by electrolytic reduction to the oxide. A recent experiment with irradiated UO_2 gave a gamma decontamination factor of 10 and a beta decontamination factor of 10^3. Contamination of the oxide product appears to occur more by occlusion than by co-deposition. The fate of plutonium is unknown.

Simultaneous dissolution of plutonium and uranium oxides was also effected by anhydrous HCl, the products being U(IV) and Pu(III). On sparging with air, plutonium precipitated as PuO_2, and uranium was converted to soluble UO_2^{+3}. This provides a means of plutonium separation from uranium. The uranium could later be recovered by electrolytic reduction.

Uranium monocarbide is considered to be a ceramic fuel material of some promise because of its reasonably good thermal conductivity. The properties of unirradiated uranium monocarbide were recently reported.[66] Irradiation of specimens of arc-melted and cast uranium monocarbide showed swelling of 0.7 to 2.5 per cent for a burn-up of 1420 Mwd per ton of uranium (0.2 per cent of the uranium). A small release of krypton could be accounted for by fission recoil from the surface.

Processing of uranium carbide fuel is being investigated at Atomics International. Oxidation of uranium carbide to U_3O_8 at 375°C in ½ atm of oxygen has been reported.[59–61] Chlorination of uranium carbide and volatilization of the uranium as a chloride have also worked. Most of the work, however, is centered on reconversion to the carbide. Conversion of the oxide to the carbide is being attempted at 2000°C, with conversions of up to 90 per cent being reported.

Miscellaneous

Several topics relating to fuel processing by pyrometallurgical procedures are discussed[67] by various authors in *Progress in Nuclear Energy, Series V, Metallurgy and Fuels*, Vol. 2. These include, among others, chapters on zone melting, melting techniques for uranium, thorium, beryllium, and uranium, and properties of basic materials. Nonaqueous processes have also been discussed in a book by Martin and Miles.[68]

An article on low decontamination of thorium alloys by induction drip melting has been published in *Nuclear Science and Engineering*.[69] This work has been covered in a previous Re-

view.[25] In the same category is an article on purification of uranium fuels by slagging.[27,70]

Several patents of interest were reported recently:

1. Method of producing hafnium-free "crystal bar" zirconium from a crude source of zirconium.[71]
2. Plutonium-aluminum alloys.[72]
3. Method of making alloys of beryllium with plutonium and the like.[73]
4. Liquid-metal compositions containing uranium.[74]
5. Nonaqueous dissolution of massive plutonium.[75]
6. Method for the reduction of uranium compounds.[76]

Aqueous Homogeneous Reactor Processing

One of the advantages of the homogeneous reactor concept is its ability to remove a sidestream from the reactor, process it, and return it to the main loop. Where such continuous processes are employed, the decontamination requirements need not be high.

The aqueous Homogeneous Reactor Test (HRT) at Oak Ridge is one of several reactors utilizing liquid fuel. A chemical processing plant has been installed alongside the reactor system. The principles involved include the accumulation and concentration of insoluble fission and corrosion products by means of a hydroclone, followed by evaporation to recover the heavy water, and dissolution of the solids in sulfuric acid for analytical control. This solution may then be cooled to reduce activity levels, and the uranium is recovered by solvent extraction.

The removal of insoluble corrosion and fission products does take care of a large percentage of the poisons likely to jeopardize reactor operations. The soluble material of greatest concern is nickel, and a development of methods for its satisfactory removal[77] is presently under way. An electrolytic method is now being tested in a full-scale unit. The cell contains a mercury cathode and a platinum-screen anode. The system including this electrolytic cell is designed to process 30-gal batches of HRT fuel solutions. Expected typical feed compositions are 0.045*M* nickel sulfate, 0.27*M* copper sulfate, 0.03*M* manganese sulfate, 0.34*M* uranyl sulfate, and 0.24*M* sulfuric acid. The nickel-removal rate was found to be a linear function of electricity passed through the solution. Current efficiency based on nickel removal was about 1 per cent. Copper was removed from the fuel solution at a rate proportional to the quantity of copper present and considerably more readily than nickel, so that copper was almost completely removed during the nickel-removal step. The removal of manganese occurred only after a considerable part of the copper and nickel had been removed from the fuel solution. Approximately 60 per cent of the uranium was reduced from the +6 to the +4 valence state during removal of 90 per cent of the nickel. Amalgam growth around each of the electrodes tended to short-circuit the cell. This was minimized by agitation of the cathodic mercury. It appeared that regeneration of the mercury by 1*M* nitric acid–1.5 per cent hydrogen peroxide might be useful.

A report on the design of the chemical processing plant for the reactor was recently released.[78] The 107-page document presents the over-all physical arrangement of the components, specific designs of process vessels including selection of construction materials, instrumentation, maintenance philosophy, and design of special tools required for maintenance.

Plant Design, Instrumentation, and Equipment Development

Instrumentation and Equipment

Some old performance tests[79] have shown that small quantities of radioactive feed solutions may be pumped successfully and that the pumping rate can be easily kept within 5 per cent of any present value. Air lifts were tested with columns ranging from 0.18 to 1 in. in inside diameter, with water, sodium chloride solution of specific gravity 1.12, and uranyl nitrate solution of specific gravity 1.45. Variables studied were diameter, height, and submergence of the columns; density, viscosity, and surface tension of the pumped liquid; back pressure on the systems; presence of suspended solids in the system; and the humidity of the operating air. Derivations of simple equations are given, and the results are presented in tabular and graphical form. Maximum and minimum pumping rates for combinations of variables and the amount of motivating air required to pump a

given quantity of liquid may be determined from these curves.

The stack effluent monitor located in the Hanford Redox facility is described, and some operational data are presented in a recently released Hanford document.[80] This instrument continuously measures and records the amounts of each of several different radioactive isotopes in the stack effluent. The total amounts of the radioisotopes emitted to the atmosphere are indicated on registers. The system was set up for the analysis of I^{131}, Ru^{103}, and Ru^{106}. Data presented for six months' operation show good agreement between the monitored samples and laboratory-analyzed samples for I^{131}.

An electrochemical cell[81] was tested and proved to have good sensitivity for determining traces of oxygen on a continuous basis in gases or gas mixtures. The cell contains a cadmium anode, a silver cathode which contacts the gas sample, and a bicarbonate electrolyte. The studies showed that this type of cell is capable of detecting changes in oxygen concentrations of less than 0.002 per cent with a deviation of about 2 per cent and that such changes could be detected in less than a minute. The life of the cell is from several weeks to several months, depending on the oxygen concentration in the gas stream, but rejuvenation is easily accomplished by replacing the spent cadmium anode with a fresh one.

A time mass flow rate device[82] has been developed that is absolute in the sense that it requires no calibration. The flow measurement is made by adding a known amount of energy to a gas and finding its resulting temperature increase. The flowmeter is essentially pressure independent and is capable of 0.1 per cent reproducibility. It is suggested that other versions of this flowmeter should be practicable over wide ranges of pressure and temperature and should be usable with a variety of gases and liquids. The appreciable pressure drop may restrict usage in certain cases.

Plant Design and Operation

In the last Review[21] reference was made to a conceptual design report for a fuel-processing facility based on processing 1000 lb of irradiated fuel per day (10,000 Mwd/ton) composed of 20 per cent total uranium (5 per cent enriched) and 80 per cent zirconium.[83] Unfortunately, in the last Review, this report was incorrectly stated to be from a Hanford source. The present reference, 83, is the correct one.

A three-stage air lift contactor[84] with a capacity suitable for the processing of 100 tons of uranium per year has been designed, built, and tested. The contactor is essentially a mixer-settler in which the streams to be contacted enter a given mixer and are sparged by air introduced through the bottom of the mixing chamber to disperse the two phases. The mixed phases flow through a slot to the settling chamber where they are separated by gravity.

The tests made consisted of testing a method of interface control, measuring the amount of air required, and measuring the aqueous entrainment in the solvent phase. Test results indicate that the energy requirements for mixing would be low, i.e., about 0.05 hp for a 46-stage, 3-contactor process for 100 tons of uranium per year. The plant air requirements combined with pilot-plant experience at Chalk River suggest that no particular difficulty in decontaminating the exhaust air to an acceptable level would be encountered. A correlation that was developed between the interfacial height and the aqueous volume fraction was tested experimentally, and the data were found to be in good agreement with theory. Aqueous entrainment in solvent does not show great dependence upon the air rate but does show a high dependence upon solvent flow rate. The use of York mesh packing decreased the aqueous entrainment and gave improved settling behavior.

The advantages claimed for this contactor were compactness, freedom from maintenance, and low energy requirements.

A new type of horizontal pulsed column is described which has been developed at the Atomic Energy Research Establishment (AERE), Harwell.[85] In principle, this can be regarded as a horizontal perforated-plate column which, unlike the pulsed mixer-settler, requires only a single pulse line irrespective of the number of extraction stages employed. Also, it preserves one of the principal advantages of a mixer-settler installation in that the concentration gradient is maintained in the event of a shutdown. Maintenance can be carried out readily when necessary. Any number of columns can be built up into a serpentine-cascade to form a compact multistage unit, thereby effecting maximum economies in building and shielding costs. Preliminary work carried out with the water-toluene-acetone system has shown the extraction

efficiency of the unit to be comparable with that of the conventional vertical type of pulsed column.

Corrosion

Corrosion is a subject which is an integral part of each process development program. Many of the current developments involve the use of chemicals which are more than usually corrosive, and in many instances programs have been set up to solve the resulting construction-material problems. In this section an attempt is made to cover the progress on such programs which has occurred in the past three to six months.

Solvent Extraction

A large variety of fuels are being designed for reactors in the power-reactor demonstration program. Each type will for the time being have to be processed in one of the plants operated for the AEC. The various plants have been assigned the responsibility of handling specific fuels. The current assignments of such fuels was given in the previous Review.[21]

In general, the highly enriched fuels will be processed at Idaho, the lower enrichment fuels (less than 5 per cent) will be handled at Hanford, thorium fuels and uranium-aluminum alloys of greater than 20 per cent enrichment will be processed at Oak Ridge, and, finally, the fuel from the fast breeder reactor in Mighigan, together with some natural elements from Canada, will be processed at Savannah River. Hanford proposes to use vacuum-melted Hastelloy-F as a "universal" construction material for handling zirconium-, stainless-steel-, and aluminum-clad fuels. Idaho will, to a large extent, utilize existing equipment: Monel for zirconium-clad fuels and Carpenter-20 for stainless-steel-clad fuels. Oak Ridge is planning to dissolve stainless-steel-clad fuel by the Sulfex process (sulfuric acid), zirconium-clad fuels by the Zirflex process (ammonium fluoride), and Nionel equipment is being constructed for these purposes. In addition, an alternate plant designed for the use of the Darex process is being constructed of titanium.

In the past several months, two compilations of results of site corrosion programs have been published. One of these is from Hanford,[86] and the other is from Battelle Memorial Institute[87] on behalf of ORNL. Many of the results have been previously presented in these Reviews, and they will not be repeated herein. But for the serious follower of corrosion data, it is a must to consult these two references.

In the Sulfex process the stainless-steel cladding of the fuel elements may become passivated. Depassivation requires the use of 12*M* sulfuric acid. Corrosion tests of Nionel made in this medium indicate that rates of attack vary from 80 to 300 mils/month. Although the period during which the dissolver would be subjected to this condition is about 5 min, this is considered high. The attack is uniform.[31,88,89]

Hastelloy-F was run through a scouting test in 6*M* sulfuric acid. In 48-hr exposures, rates were 90 mils/month in clean acid and 6 mils/month with 35 g/liter of stainless-steel corrosion products added. This does not appear to be very promising.[9]

At the ICPP, efforts are being made to dissolve homogeneously 2.5 per cent uranium–Zircaloy alloy in aqueous hydrofluoric acid by adding hydrogen peroxide to a calculated terminal concentration of 0.06*M*. Since the present zirconium processing plant at Idaho is constructed of Monel, corrosion tests were made with this construction material. Maximum corrosion observed was 0.05 mil per batch. When 0.06*M* chromic acid was used as the oxidant, this increased to 0.1 mil per batch. A Carpenter-20 pilot plant is being constructed at Idaho for the testing of some of these modifications of aqueous processing procedures for high-zirconium alloys.[90]

In a totally different approach, Idaho is investigating the dissolution of zirconium-uranium fuels in molten lead chloride (ARCO process). Corrosion tests made in lead–lead chloride mixtures at 530°C with mild steel look reasonably good, although the metal is subject to some small initial attack by the salt phase. A protective film appears to develop.[90]

In an effort to find a universal construction material for a wide variety of fuel dissolvents, a study is being made with noble-element alloys.[91] The corrodents tested consist of four different boiling-acid mixtures: (1) 2*M* hydrofluoric acid–13*M* nitric acid, (2) 15*M* hydrofluoric acid–5*M* nitric acid, (3) 2*M* hydrochloric acid, and (4) 8*M* sulfuric acid–2*M* nitric acid. The first alloy tested was 30 per cent iridium–70 per cent platinum. Observed maximum corrosion rates were less than 0.02 mil/month.

These studies will be followed by an evaluation of platinum-iridium-clad equipment for multi-reagent processing.

Corrosion tests of mild steel in neutralized aluminum nitrate wastes have further verified the low rates of attack obtained. Wastes were neutralized to a *p*H of 10 and exposed for 120 days at 60°C. Observed rates were on the order of 2×10^{-5} in./month or less.[92]

Corrosion tests of stainless-steel types 347 and 304-L, together with mild steel, have been made in neutralized zirconium wastes. The exposures were for a three-month period at 60°C. In no case did the attack exceed 1 mil/month on the stainless steel or 0.5 mil/month[92] on mild steel.

At Idaho a prototype evaporator was constructed some 10 months ago for the evaporation of first-cycle aluminum nitrate–nitric acid wastes. The 5-tube titanium bundle exposed to atmospheric boiling conditions was dismantled for inspection. Titanium surfaces were evenly covered with a dark-brown tarnish. No localized attack was observed on either the base metal or the weldments. With this observation an estimate of a five-year tube life is thought to be quite conservative.[92]

The second in a series of topical reports on corrosion studies made in the Oak Ridge Thorex pilot plant was recently released.[93] The results of the first of these was reported in an earlier Review.[18] In this continuing study several process vessels were monitored by the insertion of both stressed and unstressed, welded and unwelded specimens. These include the dissolver, the feed-adjustment tank, a catch tank, and a vapor separator. Typical results are shown in Fig. 12, and Table IV-7 includes typical operating conditions. Severe corrosion damage was encountered in the vapor phase of both the batch dissolver tank and the feed-adjustment tank. Rates of attack for stainless-steel types 304-L and 309 SCb varied from 30 to 55 mils/year in the former. Vapor-phase corrosion rates in the feed-adjustment tank ranged from 85 to 100 mils/year. None of the alloys tested underwent stress-corrosion cracking in any of the process-vessel environments, nor was there any indication of a stress-accelerated rate of corrosion attack. Corrosion in the batch dissolver and feed-adjustment tanks was significantly more severe during the development period of operation than was observed in the previously reported production period. With the exception of the solution phase in the batch dissolver tank, the rates were generally well in excess of 25 mils/year (the maximum value tentatively established for the pilot plant). Based upon continuous operation the half life of the type 309 SCb stainless-steel batch dissolver and

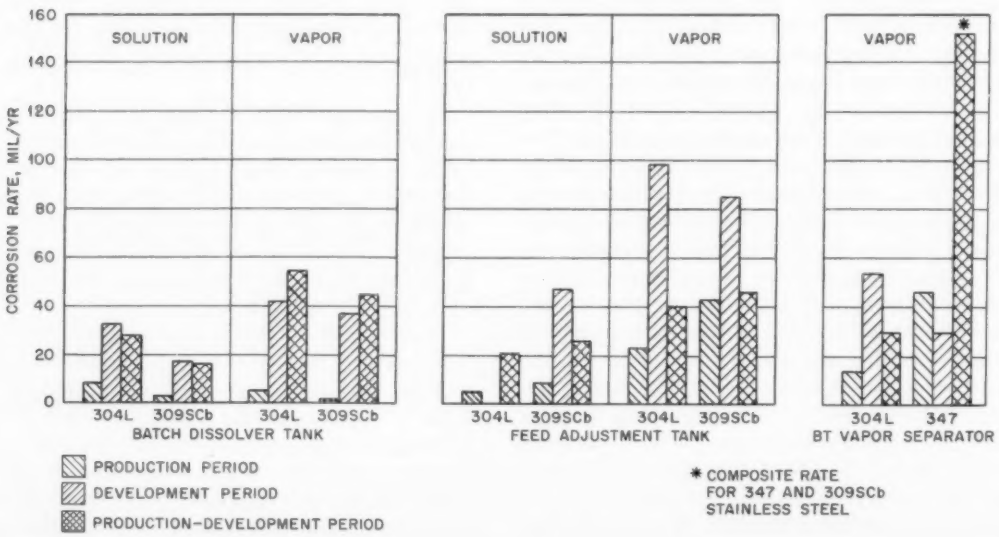

Figure 12—Maximum corrosion rates observed on stainless-steel specimens in Thorex pilot plant during production and development periods of operation.[94]

Table IV-7 TYPICAL LIQUID COMPOSITIONS IN THOREX PILOT PLANT UNIT[93]

Constituents	Composition, moles/liter					
	Dissolver		Feed-adjustment tank		Evaporator system	
	Initial*	Final	Initial	Final	Initial*	Final*
HNO_3	13.0	6.0	5.0	0.5	0.2	1.5
$Th(NO_3)_4$	0	1.0	1.0	4.0	0.025	2.0
$Al(NO_3)_3$	0.04	0.5	0.4	1.6		
$Hg(NO_3)_3$	0.04	0.0025	0.001	0.004		
Fluoride	0.003	0.0375	0.15	0.047	0.004	0.009
Temp., °C	110 to 115		110 to 115		115	
Exposure time, hr	2700		2600		5800	

*Data are taken from previous Reviews.[18]

feed-adjustment tanks was estimated to be 2.5 years each.

One of the significant containment problems associated with the handling of nitric acid in 18-8 stainless steels is the effect of the presence of chloride ions. A procedure has been developed by one of the uranium refiners to remove chloride ions from nitric acid solutions.[94]

The procedure is a simple one involving the addition of small quantities of potassium permanganate to oxidize the chloride to volatile chlorine. By using approximately three times the theoretical amount of permanganate required, it has been possible to reduce the chloride level to 20 ppm.

At the Savannah River laboratories[95] a comparison has been made between the dissolution rates of fuel materials as compared to corrosion rates of the construction material under similar circumstances. Theoretically, it should be possible via such a technique to optimize the life of the vessel relative to the number of fuel elements processed. The construction material in this case was type 309 SCb, and the fuel alloy considered was uranium–2 per cent zirconium. The results are shown in Fig. 13. For minimum corrosion of the dissolver, it would be advantageous to employ a solvent containing no more than 1*M* nitric acid. There is, however, no apparent optimum concentration of hydrofluoric acid, and the concentration selected should be the minimum that will give the penetration rates required by the production schedule.

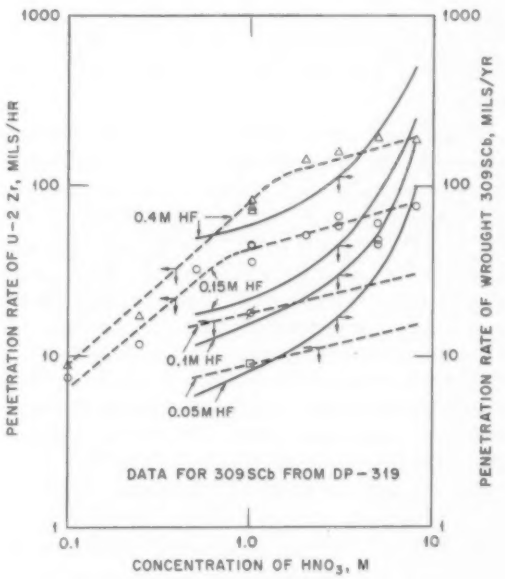

Figure 13—Penetration rates of wrought 309 SCb and uranium–2 per cent zirconium in boiling solutions of hydrofluoric acid–nitric acid.[95] ----, uranium-zirconium. ——, stainless steel.

Volatility Processing Methods

One of the newer concepts of utilizing fluoride volatility processing methods is the dissolution of a reactor fuel in a suitable solvent followed by a series of steps in fluidized beds. These steps would include calcination, hydrofluorination in a second bed, and fluorination in a third bed. The products from the last column would include uranium hexafluoride and other volatile fission-product fluorides which would be separated from the former by distillation procedures or by selective adsorption in sodium fluoride traps.

The critical step from the construction-material point of view is the fluorination column. It has been determined that temperatures on the order of 675°C are required for efficient uranium removal. A series of experiments was performed in a static bed containing zirconium fluoride through which fluorine was passed.[36] The materials included in this study were nickel and Monel. The results indicate that, under the conditions used, nickel is more useful than Monel, particularly in the laboratory where the intergranular degradation of nickel is not likely to be objectionable. It has not been established whether this is equally true for a fluid bed. No Monel specimen removed from the pilot-plant fluid-bed fluorinator has shown the degree of perforation observed in the static test. The corrosion rate of nickel in a static bed was not so high as to preclude its use under some conditions.

Fused-salt dissolution of zirconium fuels is also utilized in conjunction with fluoride volatility techniques. Zirconium fuels are dissolved in sodium fluoride–zirconium fluoride at 600 to 700°C through which anhydrous hydrogen fluoride is passed. Fluorine or some other strong fluorinating agent is passed through the resulting homogeneous melt to oxidize the tetravalent uranium to uranium hexafluoride. At ORNL a dissolver for this purpose has been constructed of INOR-8 alloy. General corrosion was not detectable after 74½ hr of hydrogen fluoride exposure. Only one point, at the interface, showed a reduction in thickness. Observed corrosion was 4 mils, which corresponds to 0.05 mil/hr. Corrosion in a new section of the dissolver was estimated from Vidigage measurements to be 0.03 mil/hr. This is higher by a factor of 10 than the rate determined by Battelle Memorial Institute on the same environment. Temperatures during the operation of the unit[96] were 700 to 670°C. The results of corrosion observed in the unit operations dissolver as compared with Battelle data are shown in Fig. 14.

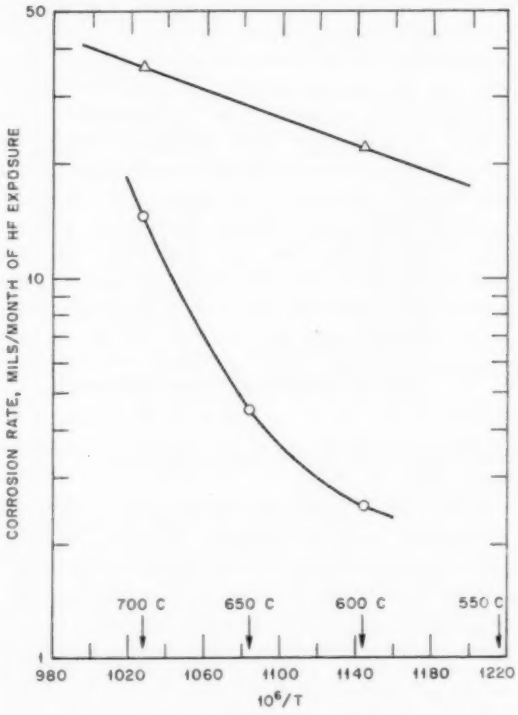

Figure 14 — Effects of temperature and melt composition on corrosion rate of hydrogen fluoride on INOR-8 dissolver.[97] Δ, ORNL data for INOR-8 runs 1 to 16, including ZrF_4 concentration effects (runs 2 to 9 were from 700 to 670°C with 0 to 18 mole % ZrF_4; runs 11 to 16 were from 660 to 535°C with 18 to 45 mole % ZrF_4). ○, BMI data for runs 23 to 25 (page 22 of BMI-1348), showing effect of temperature at one composition.

Pyrometallurgical Processing

In conjunction with the pyrometallurgical techniques being explored at ANL, a mild-steel loop containing an environment of cadmium–1.5 wt.% uranium–0.2 wt.% magnesium alloy at 550°C has been operating for 1000 hr. Radiographs taken periodically of the loop during operation did not indicate significant corrosion. Metallographic examinations revealed three locations where indications existed of slight interactions with the loop. The interaction at these points consisted of a double reaction layer on the steel wall accompanied by the presence of various intermetallic compound particles in the near vicinity of the layer. It is thought that perhaps the localized attack is due to the precipitation of either uranium or a uranium-cadmium intermetallic compound.[36]

In static tests mild steel and stainless-steel type 410 were exposed to molten cadmium and cadmium–10 wt.% zinc solutions at 700°C for 100 hr. Intergranular attack occurred in the first environment to an extent of 0.2 mil and in the second environment to 0.4 mil.[36]

In pyrometallurgical processing schemes, zinc can also be used in a manner analogous to cadmium. The latter is receiving a greater emphasis by virtue of its less corrosive nature. However, some corrosion work in the zinc system is being done. A number of Rokide refractory coatings on mild steel were tested in zinc–46 wt.% magnesium and in pure zinc. Exposures were for 100 hr at 750°C. Coatings tested included Rokide A, Rokide ZS, Rokide Z, Rokide C, and CrB_2. The Rokide designations correspond to aluminum oxide, zirconium silicate, stabilized zirconia, and silicon carbide, respectively. None of the coatings prevented the pure zinc from penetrating through and attacking the mild steel. With the exception of Rokide Z, the zinc-magnesium also penetrated the coatings and attacked the metal.[36]

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Monaco Conference

From Nov. 16 through 21, 1959, a Scientific Conference on the Disposal of Radioactive Wastes was held in Monaco under the joint sponsorship of the International Atomic Energy Agency and of UNESCO.

The Conference was attended by three separate groups—oceanographers, geologists, and those interested in handling and processing of wastes. The intention was for these three groups to explain their problems in terms understandable to the others and, recognizing the interrelatedness of the disciplines involved, to encourage a broader attack upon the problem of ultimate storage.

The subject which caused the most controversy at the meeting was the dumping of wastes into the sea. The Russians particularly objected to the practice. Other countries, especially those with close interest in the North Sea, also expressed opposition. It was clear that everyone is agreed that high-level waste should not go into the sea. There is some feeling that the British operation (at Windscale) is pushing the limits of "low-level waste" pretty hard. The British presented their position fully and defended it ably.

A Russian paper (delivered by Zimakov) described the development of a process for converting liquid wastes to solids, mixing them with various fluxing agents, and firing them to a vitreous solid. It was admitted that the solids so obtained were not completely unleachable "unfortunately." In response to questions it was stated that it was the Russian intention to use such a process in their separation plants.

Reduction to Solids

Some Russian work on the adsorption of activity onto clay and additional work on various methods of waste calcination are reported.

Adsorption on Natural Materials

A Russian paper[1] discusses the mechanism of adsorption of microscopic quantities of various ions by montmorillonite. In particular, the conditions of adsorbing $Sr^{89,90}$ by montmorillonite have been studied in detail. Various cations may be arranged in the following order according to their capacity to lower the adsorption of radioactive strontium:

$$Al^{+3} > Fe^{+3}$$

$$Ba^{++} \geq Ca^{++} > Mg^{++} \geq H^{+} > NH_4^{+} > K^{+} > Na^{+}$$

It has been shown that the adsorption of radioactive strontium by montmorillonite is an ionic-exchange process and obeys the law of mass action. The presence of the anions CO_3^{--}, SO_4^{--}, and $C_2O_4^{--}$ in a solution, which form relatively insoluble salts with strontium, does not change the mechanism of the adsorption but decreases the quantity of radioactive strontium adsorbed, apparently by forming radioactive colloids.

The process of fixing radioactive strontium on montmorillonitic clays during roasting has also been studied. Roasting at temperatures above 850 to 900°C and extending the roasting time over 1 to 2 hr do not affect the degree of fixation of radioactive strontium. In these experiments the activity lost by washing in stream and sea water amounted to about 2 per cent.

It is suggested that, up to the beginning of alteration in the crystal lattice ($T = 800°C$), the fixation is controlled by the formation of slightly soluble chemical combinations of strontium and the adsorbent. Above 800°C the process is determined by changes in the crystal lattice and by a gradual vitrification of the mineral.

At Hanford[2] the decontamination of Purex boiling tank condensate by beds of clinoptilolite as a function of solution *p*H is being studied. Small (5-g) columns of the zeolite are being

charged with waste samples adjusted to *p*H 5, 7, and 9. The adsorption of active cesium, strontium, and lanthanide fission products at rates of 4 gal/(sq ft)(min) through 22-cm columns is being studied. The system operating at *p*H 9 is still maintaining a cesium decontamination factor of 10^4 after 5700 column volume throughputs. After receiving 15,000 column volumes at *p*H 5 and 13,000 column volumes at *p*H 7, a yellowish-brown deposit was observed in the zeolite columns which tended to retard the flow. After 25,000 column volumes of *p*H 5 solution had passed through the bed, the flow was completely blocked.

Calcination

The Hanford 8-in. radiant-heat calciner[3-6] has been used on high-sulfate Purex waste to define more clearly the effect of sugar addition on sulfate destruction.[7] The results may be summarized as follows:

1. The addition of sugar results in the removal of approximately 60 per cent of the sulfate from high-sulfate waste.
2. The addition of oxygen decreases the ability of sugar to reduce sulfate. This effect was not as pronounced as in the earlier series with phosphate.
3. Addition of oxygen near the midpoint of the column resulted in increased removal of sulfate over that observed when the oxygen was added at the top of the column.

A new filter section was designed during the month, as was equipment for the study of eddy diffusivity and back mixing in the column. These latter quantities, which are important to a theoretical understanding of the spray column, will be determined by addition of helium tracer followed by sampling and analysis of the gas at selected points in the operating column.

The unit was dismantled after 200 hr of high-temperature operation. No obvious corrosion was observed.[2]

Hanford has also put into operation an experimental fluid-bed calciner[7] using simulated ICPP waste (2.0*M* aluminum nitrate, 1.0*M* nitric acid, 0.15*M* sodium nitrate) as feed and calcine from the ICPP semiworks as starting bed material. Four runs of 4 to 6 hr duration have been completed. Bed temperature in all runs was 500°C; feed rates were 10 to 20 liters/hr. Operation of the calciner has been relatively smooth and trouble-free.

Superficial fluidizing air velocities of 0.5 to 1.5 ft/sec have been tried. Minimum fluidizing air velocity is about 0.3 ft/sec, and velocities of 0.5 to 1.0 ft/sec have provided good fluidization. This compares to about 1.5 ft/sec requirements for adequate fluidization in 6-in.-diameter calciners at other sites. Untapped "product" bulk densities have ranged from 0.67 to 0.80 g/cm^3, with the density generally increasing with decreasing atomizing air rates. The untapped density of the fines removed by the scalping cyclone has ranged from 0.2 to 0.45 g/cm^3.

Exploratory studies on the fluid-bed calcination of simulated Purex ("formaldehyde killed") and threefold concentrated acid waste had first

Table V-1 HEAT-TRANSFER CHARACTERISTICS OF VARIOUS CALCINES[9]

Power level, Btu/(hr)(cu ft)	Apparent conductivity, Btu/(hr)(ft)(°F)	Center temp., °F	Temp. drop to outside of pipe, °F
	*Al_2O_3 Powder**		
2,800	0.23	264	95
6,500	0.25	462	189
10,300	0.29	669	306
13,850	0.30	820	368
	Al_2O_3 Powder†		
5,150	0.29	394	155
9,300	0.30	597	283
16,500	0.35	909	427
	Al_2O_3 Powder‡		
4,100	0.19	376	164
9,300	0.21	673	320
13,900	0.24	864	427
	Simulated IWW Calcine§		
4,700	0.055	743	553
8,400	0.049	1,292	990
10,250	0.056	1,508	1,161
	Spray-calcined ANN¶		
3,900	0.039	791	583
9,900	0.074	1,214	679

* Bulk density 1.9 g/cm^3; particle-size range from 30 to 325 mesh.

† Bulk density 1.7 g/cm^3; 100 per cent through 18 mesh, 90 per cent retained on 25 mesh.

‡ Bulk density 1.7 g/cm^3; 100 per cent through 120 mesh, 90 per cent retained on 170 mesh.

§ Produced by radiant-heat spray calciner; bulk density 0.6 g/cm^3; 99 per cent through 325 mesh.

¶ Bulk density ~0.69 g/cm^3.

been done at Argonne.[5,7] In work at ANL[8] two 6-hr runs were made at 500°C and a feed rate of 4.8 liters/hr using a 100:1 dilution of ICPP waste as radioactive tracer in the feed. One run used 120 g of sugar additive per liter. Both runs were smooth and uneventful with apparent satisfactory particle-size control and negligible particle-agglomerate formation. It may be generally concluded from the ANL studies that fluid-bed calcination of Purex waste is entirely feasible. The major problems encountered (agglomerate formation and solids build-up on the nozzles) have been partially overcome and appear solvable.

At Hanford the heat-transfer characteristics of various granular materials were determined in equipment designed to approximate the uniform generation of heat expected in a container of calcined waste.[9] Material to be tested was placed in a 4-in.-diameter pipe 2 ft long and was heated by Nichrome wires on ½-in. equilateral triangular spacing parallel to the cylinder axis. Thermocouples provided a means for determining the temperature profile in a radial plane midway down the pipe. The results obtained in this work are given in Table V-1.

Removal of Specific Isotopes

Further work is reported on a solvent-extraction method of recovering isotopes mentioned in a previous Review.[5,7] A batch experiment was run to test operability of the di-2-ethylhexyl phosphoric acid (D2EHPA) strontium recovery process with actual Purex first-cycle waste. One volume of waste was mixed with one volume each of 1*M* tartaric acid and 5.8*M* sodium hydroxide to yield a nearly neutral solution. This solution was contacted with an equal volume of 0.3*M* D2EHPA, 0.14*M* TBP, Amsco solvent. After stirring for about 1 min, the phases required about 15 min for complete separation. No solids were detected in either phase, even after standing overnight. Ninety-five per cent of the strontium was extracted into the organic phase along with two-thirds, or more, of the cerium, yttrium, and rare earths, and 11 per cent of the cesium-barium. Extraction of ruthenium and zirconium-niobium was negligible. No solvent superior to D2EHPA has been found. Work on this process is being suspended at Hanford.[2]

The behavior of strontium in the rare-earth

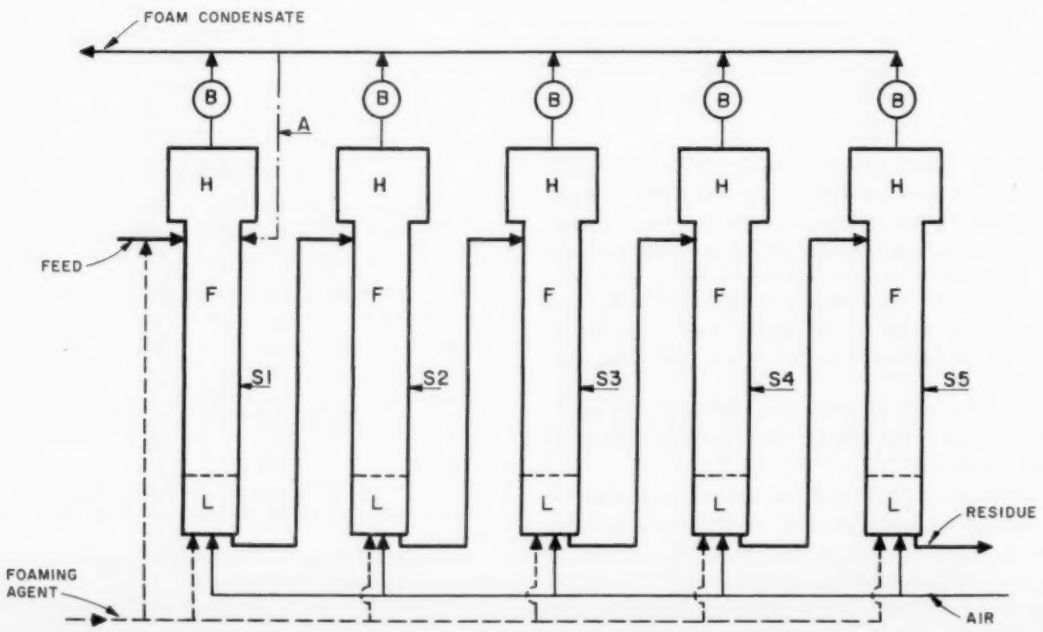

Figure 15—Multistage (series column) operation.[11] *L*, liquid. *F*, foam. *B*, foam breaker. *H*, expanded head.

double-sulfate process[5] is being studied at Hanford in an effort to devise a strontium-recovery scheme which will not require precipitation and centrifugation of the iron which is present in such large amounts in first-cycle waste.[7] The fraction of the strontium that coprecipitates with the rare earths can be greatly increased by increasing the sulfate concentration to a value higher than is required for rare-earth recovery alone. Strontium recoveries of 75 to 80 per cent were obtained by butting the sulfate content of synthetic waste to 3*M* with sodium sulfate, partially neutralizing to *p*H 0, and digesting for 2 hr at 80 to 100°C. Without partial neutralization, but with the same sulfate concentration, strontium recovery was only about 45 per cent.

More recent work on the rare-earth double-sulfate process has shown that it is possible to obtain over 90 per cent of the cerium and promethium and at least 80 per cent of the strontium as separate concentrated purified product fractions.[2] The use of lead carrier in the concentration range 0.01*M* to 0.03*M* assures coprecipitation of 85 to greater than 99 per cent of the strontium in the rare-earth double-sulfate precipitation step at sulfate concentrations of only 1*M* to 1.5*M*.

The process called "foam separation," described in an earlier Review, has been demonstrated on a multicolumn basis.[10,11] Using five columns set up as shown in Fig. 15, decontamination factors of 10^9 have been demonstrated[12] for the removal of strontium from a synthetic "Purex type" waste.

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PRODUCTION OF URANIUM, THORIUM, PLUTONIUM, AND THEIR COMPOUNDS

Uranium

Uranium Trioxide

The production of uranium trioxide was originally accomplished by batch calcination of uranyl nitrate in agitated denitration pots. With one exception (the Hanford continuous-trough process)[1] this method is still the only one in large-scale use in this country. The fluidized-bed process is under pilot-plant development at Mallinckrodt.[2] Although the most desirable continuous denitration reactor may well be one which has been specifically designed for this purpose, continuous operation of the existing denitration pots has recently been considered as a promising approach to process improvement at the National Lead Company of Ohio production center.[3] This scheme involves the continuous introduction of uranyl nitrate into the agitated pot and simultaneous withdrawal of the oxide product.

The most attractive feature of the continuous pot method of denitration is the absence of the extreme thermal cycling which is the major cause of pot failure. Since the pot charge is maintained in the dry state, scale formation on the inner surface of the reactor should be avoided, thus allowing lower pot skin temperatures than those currently experienced. The suitability of the oxide as a feed for the uranium tetrafluoride production plant constitutes a major unknown. As has been noted for other continuously produced oxides, the reduction and hydrofluorination activities of continuous pot oxide are expected to be lower than that of the current pot powder.

To demonstrate the operational feasibility and the productivity of continuous pot calcination and to determine the characteristics of the oxide produced in this system, experiments were performed in a laboratory denitration pot system. Molten uranyl nitrate [80 per cent $UO_2(NO_3)_2$] was introduced below the surface of a heated, agitated bed of uranium trioxide through a steam-cooled feed tube. The agitation rate was 25 rpm, and the average bed temperature was about 275°C. For a pot charge of 3300 g of oxide, a typical feed rate was 38 ml/min. Product was withdrawn intermittently through a side discharge tube.

The data obtained in these experiments indicate that, with adequate auxiliary facilities, uranium trioxide can be produced continuously in the conventional denitration pots at rates equal to, or greater than, those obtained by batchwise calcination. The oxide produced consists of granular agglomerates which are free-flowing and have a low surface area and high bulk density. Reduction and hydrofluorination activities are both lower than those of powder produced by batch denitration. Further work in plant-scale equipment is planned.

Another method for overcoming the deficiencies of the current batch denitration process is the continuous conversion of uranyl nitrate in aqueous solution by precipitation with aqueous ammonia to produce ammonium diuranate (ADU). This process is expected to improve product uniformity, purity, and performance in subsequent reduction and hydrofluorination. A discussion of the semiworks production of ADU was presented in a previous Review.[4] More recently an engineering evaluation of the semiworks performance has been issued.[5]

The operating conditions for the semiworks agreed closely with the design conditions for the process. Approximately 1 ton of product per day was obtained over a period of nearly six months. A 75 per cent on-stream factor and a process yield of nearly 90 per cent were realized; considerable improvement in these factors is believed possible on a full-plant scale. The product has been shown to be uniformly reactive and to possess a tap density of 2.54 g/ml. Significant decontamination of several impurities, notably sodium and iron, has been shown.

Uranium Tetrafluoride

The production of uranium tetrafluoride is accomplished on a large scale by the hydrofluorination of uranium dioxide in horizontal screw-agitated reactors. Three 20-ft-long reactors are operated in series with countercurrent flow of solids and gas. Although such reactors have been operated successfully for many years, two factors have recently contributed to operating difficulties: (1) higher throughputs associated with the advent of the fluid-bed reduction reactors, and (2) operation with lower hydrogen fluoride excess and with feeds of variable reactivity. Plugging and sintering effects due to excessive reaction temperatures sometimes result in low conversions, low on-stream factors, and high maintenance costs. Since the reactors are cooled only by moderate air cooling, it appears that an improved external cooling system should lead to further operational improvement.

A reactor cooling system that embodied high heat-transfer rates, flexibility in location and amount of cooling, and low cost was designed and installed on one reactor bank at the National Lead Company of Ohio plant.[3,6] Cooling coils of copper tubing were applied to certain high-temperature zones of the first two reactors in the bank. To aid heat transfer, the coils were metalized with copper and then oversprayed with stainless steel to retard corrosion. A mixture of steam and water separately metered was used as the cooling agent.

Plant tests showed that near-optimum control of temperatures could be achieved with this cooling system. The experimental reactor bank experienced (1) greatly reduced downtime due to plugging by the solids, (2) substantial relief from high screw torques (lessening the opportunity for severe screw damage), and (3) sustained high production rate (50 per cent above normal), even when operating with feeds which in uncooled reactor banks would normally lead to operating difficulties and low conversions. As a result of this study, five additional reactor banks were modified to include cooling of the first reactor. The tests also showed that efficient reactor cooling permits the processing of uranium trioxide feeds containing higher concentrations of impurities (e.g., sodium) which normally aggravate the solids sintering problem. It has been possible to raise the plant specification for sodium from 20 to 30 ppm.

Uranium Hexafluoride

At the Portsmouth (Ohio) Gaseous Diffusion Plant, operated by Goodyear Atomic Corporation, uranium recovery operations are carried out which involve the conversion of uranosic oxide (U_3O_8) to uranium hexafluoride. Since the uranium is enriched and the quantity is relatively small, a direct reaction of the oxide with elemental fluorine is employed instead of the conventional three-step operation involving reduction, hydrofluorination, and fluorination. Small inclined-tube reactors equipped with vibrators which caused the oxide to move slowly down the length of the reactor were used. Because of the high heat of reaction the throughput was low, less than 1 lb of oxide per hour.

To improve the economics of the process, an oxide fluorination tower reactor was designed and installed in a pilot plant for testing.[7] This 3-in.-diameter reactor was similar in construction to the larger tower reactors used for the conversion of uranium tetrafluoride to uranium hexafluoride[8] and was very similar to the experimental and semiproduction units developed and operated at the Oak Ridge Gaseous Diffusion Plant. The oxide was fed from a hopper to the tower by a screw feeder. The fluorine and oxide entered at the top and flowed concurrently down through the tower. Steam inside of copper coils was used for cooling. The unreacted or partially reacted oxide was collected in an ash receiver at the bottom. Fine solid particles were removed from the gas stream by an electrostatic precipitator and a porous-metal-tube filter. The uranium hexafluoride was collected in cold traps.

For optimum operation of the 8-ft-long tower, the oxide feed rate was 15 lb per hour with a minimum fluorine excess of 75 per cent. The material collected in the tower ash receiver represented 6 to 10 per cent of the total amount of uranium fed during a run. The ash, combined with an equal weight of oxide, can be fed back to the tower. The electrostatic precipitator was capable of collecting up to 92 per cent of the solids in the gas stream, the remainder being removed by the tube filter. The uranium in the deposits from the filter and precipitator was contaminated by the impurities present in the oxide feed. This uranium can be recovered by conventional wet decontamination methods. It was estimated that the conversion rate to hexafluoride could be increased from 4 lb of uranosic

oxide per man-hour with the inclined-tube reactors to 10 lb per man-hour using the tower reactor.

Conversion of Uranium Hexafluoride to Uranium Dioxide

Preliminary development work at ANL on a continuous process for the conversion of uranium hexafluoride to uranium dioxide by reaction with a mixture of hydrogen and steam was described in an earlier Review.[2] The purpose of this work is to develop a more economical process for large-scale production of enriched uranium dioxide for nuclear fuel. Because of the encouraging results obtained in the initial work in a 1½-in.-diameter fluid-bed reactor, a 3-in.-diameter reactor of similar design has been installed and operated.[9] In this process, gaseous uranium hexafluoride is injected into a bed of uranium dioxide fluidized with steam and hydrogen at approximately 600°C. Feed rates as high as 160 lb of uranium hexafluoride/(hr)(cu ft of static bed volume) have been used with complete conversion of the gaseous hexafluoride to solid compounds. However, the solid product has been incompletely converted to uranium dioxide, necessitating a second stage to decompose the fluorides and complete the conversion.

The reaction apparently proceeds in two steps. The first is a rapid gas-phase reaction in which the hexafluoride is converted to uranyl fluoride and uranium tetrafluoride. The second is a slower gas-solid reaction in which the fluoride compounds are converted to dioxide. At low feed rates the reaction can be virtually completed in a single stage, but at high feed rates a second stage is required to allow sufficient residence time to complete the conversion. In batch fluidized experiments, a residence time of about 2 hr in the second stage reduced the fluoride content of the intermediate product from 0.4 per cent to about 0.03 per cent. Experiments to evaluate the sintering properties of the product for the preparation of high-density uranium dioxide fuel are planned.

Other studies are being carried out at the Oak Ridge Gaseous Diffusion Plant with the objective of recovering hydrogen fluoride from depleted uranium hexafluoride.[10] The process is similar to that described above except that low excesses of steam are used to produce a hydrogen fluoride product which is low in water content. In this case complete conversion of the solid product to dioxide is not important. A 6-in.-diameter fluid-bed reactor has been used for pilot-plant studies. In an initial run at 28 lb of uranium/(hr)(cu ft of bed), the system was operated continuously for 60 hr without difficulty. The in-bed temperature was about 1300°F, and the solids retention time was approximately 5 hr. Fluoride recoveries of 96 per cent (i.e., around 2 per cent in product) were attained with average hydrogen fluoride concentrations in the outlet condensables of about 87 per cent. One notable difference from the results of the ANL work is that the solid product was close to U_3O_8 rather than UO_2 in composition. A later run encountered difficulties due to production of fine solid particles with resultant loss of fluidity of the bed. An explanation for this behavior is being sought.

Uranium Metal

Uranium metal is produced by the bomb reduction of uranium tetrafluoride with granular magnesium in a closed steel vessel lined with recycled magnesium fluoride slag. The molten uranium metal collects below the magnesium fluoride slag as a "derby." To control and maintain high crude derby yields and uranium quality in the production operations, it is necessary to know the effects of variables such as the excess of magnesium, the uranium tetrafluoride purity, and the operating conditions. In plant practice a 3.25 per cent magnesium excess is used to reduce green salt containing 93.0 per cent uranium tetrafluoride or more. To determine whether yields and quality might be economically improved, a statistically designed experiment was performed with small-scale bomb reduction equipment whose dimensions were proportionate to that of production equipment.[11]

The evaluation consisted of 54 reduction runs. Three different purities of green salt and three different magnesium excesses (2, 4, and 6 per cent) were studied. Vessel surface temperatures of 650, 675, and 700°C were also evaluated. Under the conditions of the experiments, magnesium excess had the greatest effect on crude yield. Six per cent magnesium excess produced yields significantly higher than did 4 or 2 per cent excess. Yields also increased with green-salt purity, but there was an interaction between this variable and the magnesium ex-

cess; increasing the purity had the greatest effect when magnesium excess was low and the least effect when magnesium excess was high. The best uranium metal quality was obtained with green salt containing 95.5 per cent uranium tetrafluoride or more. No significant difference in crude yields was found between the preheat temperatures.

In other studies the effect of the concentrations of uranium dioxide and uranyl fluoride in green salt was evaluated.[3] This study was made by examining 603 plant-produced derbies and correlating the amount of slag adhering to the derby with the concentration of the above compounds. Other data have suggested that the greater the amount of adhering slag, the poorer the metal quality of the finished product. A definite linear correlation was found between the concentration of uranium dioxide and the percentage of the derby covered by slag. Slag adherence increased with uranium dioxide content of the green salt. No correlation between uranyl fluoride concentration and slag adherence could be found.

Uranium Recovery from Slag

Reference has previously been made to the development of new solvent-extraction processes for purification of uranium contained in slag and liner residues from uranium tetrafluoride reduction operations.[12] The attractive feature of the new solvents is their ability to extract uranium from sulfuric acid solutions obtained from leaching the slag. Older extraction processes, which depended on a nitrate system, required the use of more expensive nitric acid for leaching. Prior to development of the newer solvent systems, an ion-exchange process was placed in operation at the Oak Ridge Y-12 Plant, where enriched uranium is processed and recovered from various residues.[13] The ion-exchange process, which replaced the previously used nitric acid solvent-extraction system, has been in operation since 1957. This method was chosen to take advantage of the lower reagent costs of sulfuric acid and commercial ammonium nitrate, elimination of costly complexing agents, adaptability of the ion-exchange process to unclarified feed solutions, and the suitability of the column contactor design to limitations of nuclearly safe process geometry.

The operation involves the roasting and size reduction of the solid gangue material (mostly magnesium fluoride) prior to sulfuric acid digestion under controlled conditions of pH, temperature, and oxidation potential. The resulting uranyl sulfate slurry is partially clarified to 2 to 10 vol.% solids using conventional process equipment and is pumped to the contactor. A Higgins semicontinuous moving-bed contactor is used. The uranium is absorbed as an anionic uranyl sulfate complex and is recovered in purified and concentrated form by elution with an acidified ammonium nitrate solution. The product is precipitated with ammonium hydroxide, and the resulting ammonium diuranate cake is calcined to uranosic oxide (U_3O_8).

The reader is referred to the original report[11] for a detailed description of the process and equipment along with a discussion of the process variables. Small-scale tests of equipment and resin characteristics are also presented by the authors.

Uses for Depleted Uranium

The development of commercial markets for the large quantities of depleted uranium which are accumulating as a by-product of gaseous-diffusion operations would improve the economics of the over-all U^{235} production. Development of fast "breeder" and converter reactors, in which U^{238} would serve as the fertile fuel, and of shielding materials to replace metals such as lead, may increase the outlets for depleted uranium in the future. An extensive literature search on the subject of new and expanded nonnuclear uses of uranium and its compounds was conducted by the MIT Practice School at Oak Ridge.[14] A comparison of chemical and physical properties and consumption figures for uranium and the similar metals, chromium, lead, molybdenum, tungsten, and vanadium, was made as a guide to the possibility of replacing these metals with depleted uranium in some uses. The following uses were suggested as showing promise for consuming substantial quantities of the depleted material: (1) uranium as a catalyst in the organic and petrochemical industries, (2) as a component of various alloy systems, and (3) as a replacement for lead in such applications as ammunition, weights, and ballast. Depleted uranium, quoted at $5 per pound, is in a poor economic position to compete with lead, selling at $0.13 per pound, but could be competitive with chromium ($1.29 per pound), molybdenum ($3.55 per pound),

tungsten ($3.54 per pound), and vanadium ($1.28 per pound as V_2O_5). However, since the price of depleted uranium is AEC-controlled, it is subject to revision by the Commission at any time.

Thorium

Thorium and Thorium-Uranium Oxides

Several reactors have been proposed which utilize a thorium oxide slurry, or a thorium oxide–uranium oxide mixture, as a blanket material or as a core material. These oxides are therefore being prepared at ORNL on a routine basis in 150-lb batches for experimental use.[15] The thorium oxide is formed by calcination of thorium oxalate precipitated from a solution of thorium nitrate under carefully controlled conditions to produce material in the particle-size range of about 1 to 5 μ. The bulk of the past production has been pure thorium oxide; however, oxides have been prepared with uranium-to-thorium ratios ranging from 0.005 to 0.16. Current production is primarily oxide with a uranium-to-thorium atomic ratio of 0.03.

Conventional equipment is used, but precautions are taken to prevent ingestion of thoria by operating personnel. Thorium is a long-lived alpha emitter and is biologically hazardous. Closed tanks are used, and other pieces of equipment are covered with metal or plastic glove boxes.

The precipitated thorium oxalate is filtered and calcined at temperatures up to 650°C for several hours. Uranium is added to the calcined oxide by deposition from basic uranyl carbonate. A uranium solution is prepared by dissolving ammonium diuranate in excess ammonium bicarbonate. Thorium oxide is added, and the resultant slurry is boiled to decompose the excess ammonium bicarbonate and deposit all the uranium on the thoria in the form of uranyl carbonate. The slurry is then filtered, washed, and calcined as before.

Particles of thoria and thoria-urania calcined at 650°C do not have sufficient strength to resist particle-size degradation in reactor applications. Therefore the oxide is finally calcined at higher temperatures. Plain thoria is calcined at 1600°C, but thoria-urania is calcined at 1050°C to avoid sintering of the mixed oxide which results in particles larger than the desired size.

To remove the particles which are larger than 10 μ (about 2 per cent of the total), a simple settling-decantation system is used. The oxide is slurried with water, the large particles are allowed to settle, and the remaining material is removed by decantation. The solids are then separated in a basket centrifuge and finally dried at 650°C.

The thorium oxide particles produced in the above process have cubic and platelet shapes. In some reactor applications, spherical particles are desirable in order to reduce erosion of equipment and to reduce particle degradation. In connection with the development of a boiling slurry reactor, a procedure has been developed on a small scale at ANL by which spherical thoria particles have been prepared by jetting nitrate-stabilized thorium hydroxide sol into gaseous ammonia.[9] The sol is prepared by addition of ammonium hydroxide to a concentrated thorium nitrate solution. This sol is then sprayed through an atomizing nozzle into a chamber filled with ammonia gas. The spherical droplets solidify by precipitation of thorium hydroxide and are collected at the bottom of the chamber. Ammonium nitrate is removed by leaching with ammonia water, after which the particles are dried and calcined. The particles, when examined microscopically, have a spherical shape and diameters in the range of several microns.

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